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## Monolith Catalysts for Closed-Cycle Carbon Dioxide Lasers

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submitted by

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# "Monolith Catalysts for Closed-Cycle Carbon Dioxide Lasers"

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## ABSTRACT

The general subject area of the project involved the development of solid catalysts that have high activity at low temperature for the oxidation of gases such as CO. The original application considered was CO oxidation in closed-cycle CO<sub>2</sub> lasers. The scope of the project was subsequently extended to include oxidation of gases in addition to CO and applications such as air purification and exhaust gas emission control. The primary objective of the final phase grant was to develop design criteria for the formulation of new low-temperature oxidation catalysts utilizing Monte Carlo simulations of reaction over NASA-developed catalysts. This work resulted in a paper published in the Journal of Catalysis.

## FINAL REPORT

### OBJECTIVE

The primary objective of the grant was to develop design criteria for the formulation of new low-temperature oxidation catalysts utilizing Monte Carlo simulations of reaction over NASA-developed catalysts. This work resulted in a paper published in the Journal of Catalysis in. A copy of this paper follows and serves as the main body of this final report. The computer programs used in this work are listed in two appendixes to this final report.

## Two-Component Catalysts for Low-Temperature CO Oxidation: A Monte Carlo Study

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The reaction of CO and O<sub>2</sub> at low temperature over composite, noble-metal/reducible-oxide catalysts is simulated using Monte Carlo techniques. High activity for CO oxidation can be obtained over a composite material composed of a highly interspersed mixture of one type of site that adsorbs CO and O<sub>2</sub> and another type of site that adsorbs O<sub>2</sub> without significant CO inhibition. For example, the rate over Pd under 1% of an atmosphere of CO at room temperature is predicted to increase 10 orders-of-magnitude with addition of 1% of surface sites which adsorb O<sub>2</sub> but not CO. For most reaction rules and parameter values, a roughly 50-50 mixture of the two types of sites gives the greatest activity per unit total surface area. This result is determined by the reaction stoichiometry and the fact that the two reactants primarily adsorb separately on the two different types of sites. In a randomly distributed mixture, the two types of sites have widely differing activities which depend on the local site configurations. The local site configurations of the most active sites in a random surface are similar to site configurations found in a search for optimal configurations. The site configurations found in the search for optimal configurations were about 20% more active than the random surfaces of the same overall composition. This relatively small increase may be due to the simple steric requirements of CO and O<sub>2</sub> adsorption. We expect that similar searches for optimal site configurations will be more fruitful for reactions with more complex steric requirements. © 1993 Academic Press, Inc.

### INTRODUCTION

For most of us who are familiar with conventional CO oxidation catalysts which are active only at temperatures above about 150°C, observation of rapid CO oxidation at room temperature can be startling. In our laboratories, for example, we have measured, at room temperature, 56% conversion of a stoichiometrically balanced, atmospheric-pressure mixture of 1% CO and 0.5% O<sub>2</sub> in N<sub>2</sub> flowing at 1.2 cm<sup>3</sup>/s over 0.2 g of Au/MnO<sub>2</sub> (1). Au/MnO<sub>2</sub> and related materials are some of the few heterogeneous catalysts with activities at ambient conditions which may approach those of biological catalysts. The objective of the work presented here is to help develop an under-

standing of how these heterogeneous catalysts are able to oxidize CO at ambient and subambient temperatures.

There are several applications in which the catalytic oxidation of CO near ambient temperature is desirable. One such application is removal of CO as a contaminant of breathing air in enclosed spaces such as submarines and space vehicles and in burning structures or mines (2). Another is oxidation of CO in automobile engine exhaust during cold starts (3). A third is regeneration of CO<sub>2</sub> in transversely excited atmospheric pressure (TEA) CO<sub>2</sub> lasers (4, 5). Stoichiometrically balanced mixtures of CO and O<sub>2</sub> are generated during the operation of CO<sub>2</sub> TEA lasers through the decomposition of CO<sub>2</sub> by the electrical discharge that initiates the lasing process. Consumption of CO<sub>2</sub> and buildup of O<sub>2</sub> degrades the performance of

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such a laser. A CO oxidation catalyst that operates under low-temperature conditions is desirable for the development of closed-cycle or sealed CO<sub>2</sub> TEA lasers, which have applications such as mapping of earth's wind patterns from space by laser Doppler anemometry and remote sensing of environmental pollutants by infrared spectrometry (6).

The reaction between CO and O<sub>2</sub> proceeds at a negligible rate over metal catalysts near ambient temperature, even though the reaction is thermodynamically favored and there are several metals, including Pt and Pd, which can chemisorb both species and, thus, should permit a Langmuir-Hinshelwood-type reaction mechanism to occur (7). The explanation frequently given for the lack of reaction under these superficially favorable conditions is that CO requires only a single vacant adsorption site and O<sub>2</sub> requires two adjacent vacant sites, so that a clean surface exposed to a mixture of CO and O<sub>2</sub> quickly becomes covered with CO, which prevents O<sub>2</sub> adsorption, except at low CO-to-O<sub>2</sub> ratios (8). Only at elevated temperatures, where CO desorption becomes significant, do enough adjacent adsorption-site pairs become available to allow significant O<sub>2</sub> chemisorption and reaction to occur.

A demonstration of the foregoing explanation was presented by Ziff *et al.* (8). Using a simple stochastic (Monte Carlo) model which assumed equal sticking probabilities for CO and O<sub>2</sub> and neglected CO desorption, they showed that chemisorption and reaction of both CO and O<sub>2</sub> could occur on a uniform surface only when the ratio of the partial pressures of CO to O<sub>2</sub>,  $P_{\text{CO}}/P_{\text{O}_2}$ , fell between 0.59 and 1.0. At higher  $P_{\text{CO}}/P_{\text{O}_2}$ , including the stoichiometrically balanced case where  $P_{\text{CO}}/P_{\text{O}_2} = 2$ , the surface becomes covered with CO. If the sticking probability of CO is greater than that of O<sub>2</sub>, which would be the case for a Pt surface, these partial-pressure ratios would be shifted downward and further away from stoichiometry.

The treatment by Ziff *et al.* is quite general and should apply to any single-component catalyst in which a species requiring only a single adsorption site is to be oxidized by O<sub>2</sub>. A number of other workers have studied the CO + O<sub>2</sub> reaction, or the general A + B<sub>2</sub> reaction, over surfaces using Monte Carlo (9-18) and cellular automaton simulations (19). Ertl and co-workers have used cellular automaton simulations to study the participation of Pt surface reconstruction in rate oscillations during CO oxidation (20, 21). Related Monte Carlo studies have been made of the general A + B reaction over surfaces (22-30). Monte Carlo simulations are required in order to study the kinetics of surface reactions in which adsorbed species are not randomly distributed over the surface; traditional kinetic models using algebraic rate equations assume such random distribution.

The fact that a CO oxidation catalyst must perform two distinct functions, adsorption of CO and dissociative adsorption of O<sub>2</sub>, suggests that a "composite material" composed of an intimate mixture of two different materials, each with optimal properties for one of the two catalytic functions required, would have significant low-temperature activity (31). In such an ideal "composite catalyst," CO and O<sub>2</sub> would not compete for the same adsorption sites and, thus, CO inhibition of low-temperature CO oxidation would be eliminated.

A class of composite materials is currently under development for application as low-temperature CO oxidation catalysts in CO<sub>2</sub> TEA lasers and in breathing air purification. We have given the term "noble-metal/reducible-oxide" (NMRO) catalysts to this class of catalytic materials (32). Examples include Au/MnO<sub>2</sub> (33), Au/Fe<sub>2</sub>O<sub>3</sub> (34), and Pd/SnO<sub>2</sub> (35, 36). These materials have greater activity and stability than the conventional low-temperature CO oxidation catalyst, Hopcalite, which is a mixture of Cu and Mn oxides with small quantities of other oxides (37). In each of the NMRO catalysts, neither of the separate compo-

nents have appreciable activity for CO oxidation at low temperature and, thus, a synergistic interaction is present in the two-component materials. Although the mechanisms of CO oxidation over these materials are not known in detail (32), a probable general explanation for their low-temperature activity is that the noble metal chemisorbs CO and the reducible oxide provides sites that dissociatively adsorb  $O_2$ . There are also indications that surface hydrogen or hydroxyl participates in the dissociative adsorption of  $O_2$  and the oxidation of adsorbed CO at low temperature (38).

One barrier to our understanding of the mechanism of CO oxidation over these composite catalysts is that we do not know the surface structure and composition of these materials. Discrete noble-metal particles are present in many catalyst formulations. Recently, Brosilow *et al.* (9) adapted the model of Ziff *et al.* (8) to investigate the effect of a reducible-oxide support on the oxidation of CO over noble-metal particles. The effect of the reducible-oxide support was simulated by holding the coverage of adsorbed oxygen at saturation at the perimeter of noble metal particles. Near a stoichiometric ratio of CO and  $O_2$ ,  $P_{CO}/P_{O_2} = 2.1$ , the reaction rate was nonzero for a distance of three or four noble-metal lattice sites with penetration from the perimeter into the noble-metal particle; the rate would be zero everywhere on the particle in the absence of the reducible oxide at the perimeter. At lower CO to  $O_2$  ratios, the effect of the reducible oxide penetrates further into the noble-metal particle. These results suggest that very small noble-metal particles would provide the highest rate per noble-metal surface atom, especially for stoichiometric mixtures.

Enhanced reaction at the perimeter of noble metal particles in contact with a reducible-oxide support is not the only possible reason for the enhanced activity of NMRO catalysts. The activity of Pt/ $SnO_2$  is increased by reducing pretreatments, and Hoflund and co-workers (39, 40) reported

that such pretreatment leads to the formation of Pt-O-Sn,  $Pt(OH)_2$ , metallic Pt and Sn, and Pt-Sn alloy. In related work, Oh and Carpenter (41) found that a Pt-Rh catalyst which contained bimetallic Pt-Rh particles had enhanced activity for CO oxidation. They proposed that Rh provided sites favorable for  $O_2$  adsorption near CO adsorbed on Pt. Rh may have been present as a reducible oxide in the Pt-Rh bimetallic particles, making this catalyst a member of the NMRO class of materials. Logan and Paffett (42) studied the CO oxidation activity of a 50-50 Pd-Sn surface alloy. They found that Pd-Sn had higher activity than pure Pd but also found that the Sn oxidized to form a partial  $SnO_x$  overlayer. Work with Rh/ $TiO_2$  has demonstrated that the unique activity of this material after high temperature reduction pretreatment is related to the presence of  $TiO_x$  overlayers covering much of the surface of the Rh particles (43, 44). Although the unique activity in these cases may result from reaction at the interface between the noble-metal and oxide overlayers, this interface may be complex and the noble-metal and reducible-oxide components highly interspersed.

In this work we investigate the reaction of stoichiometric mixtures of CO and  $O_2$  over highly interspersed mixtures of noble-metal and reducible-oxide sites using Monte Carlo simulations. We demonstrate that a two-component catalyst, in which one component chemisorbs CO and the second component chemisorbs  $O_2$  but does not significantly chemisorb CO, makes possible the low-temperature reaction of stoichiometric mixtures of CO and  $O_2$ . We suggest that this feature accounts for the pronounced low-temperature activity of NMRO catalysts which readily catalyze the reaction of stoichiometric mixtures of CO and  $O_2$  at room temperature and below (4, 34). Monte Carlo simulations are performed in order to investigate the effects of different  $O_2$  adsorption rules, the effect of changing the  $O_2$  adsorption probability, the kinetic orders of the reaction, and the effects of changing the CO

desorption probability. Finally, a search is made for optimal configurations of surface sites as a first step towards the rational design of composite catalysts. With the exceptions of the study of uniform surfaces with heterogeneous boundaries by Brosilow *et al.* (9) and the study of uniform surfaces with defects by Vlachos *et al.* (15, 45), this is the first Monte Carlo study, of which we are aware, of catalytic reaction over nonuniform, multicomponent surfaces.

#### REACTION MODEL

Noble-metal sites which adsorb CO are referred to in this work as  $\alpha$  sites and the reducible-oxide sites which adsorb  $O_2$  are referred to as  $\beta$  sites. Previous Monte Carlo simulation work on uniform surfaces has referred to the  $CO + O_2$  reaction as a member of a general class represented by the reaction  $A + B_2$ . The labels  $\alpha$  and  $\beta$  have been used previously to distinguish between different sites on catalyst surfaces identified during thermal desorption experiments (46). Thus, the cases studied here can be referred to as examples of the general  $A + B_2$  reaction over a two-component,  $\alpha$ - $\beta$  surface.

The identity of individual  $\beta$  sites is not specified in the Monte Carlo simulations. In  $Pt/SnO_2$ , for example, actual individual  $\beta$  sites might consist of one or more of the following:  $(Sn)_z$ ,  $(SnH_x)_z$ ,  $(SnO_x)_z$ ,  $(SnO_xOH_y)_z$ ,  $(SnO_xH_y)_z$ ,  $(SnOH_y)_z$ , etc. Interspersion of noble-metal and reducible-oxide materials should lead to modification of the properties of each material. Such modifications are not explicitly considered here, although they could be studied by determining the effect of varying the adsorption, desorption and reaction probabilities assigned to each site. Rather, these simulations mainly probe geometric effects such as the effects of changing the relative positions of the two sites in a surface.

The main loop in the simulation program is shown in Fig. 1. This program was developed in order to consider sets of parameter values where adsorption and reaction probability values are within several orders-of-

magnitude of each other. The adsorption, desorption, and reaction probabilities are independent of surface coverage. The  $O_2$  sticking probability is the same for all allowed site pairs, and the reaction probability is the same whether the O atom is adsorbed on an  $\alpha$  site or a  $\beta$  site. Surface diffusion is not described. A lattice of square sites was used in all simulations.

The following "base set" of parameter values was used below, except where specified otherwise:

(a) CO sticking probability (probability that a gas phase CO molecule striking a vacant  $\alpha$  site will adsorb):  $p_1 = 1$ ;

(b)  $O_2$  sticking probability (probability that a gas phase  $O_2$  molecule striking a vacant pair of sites that correspond to the specified set of  $O_2$  adsorption rules—e.g.,  $\alpha$ - $\alpha$ ,  $\alpha$ - $\beta$ ,  $\beta$ - $\beta$ —will adsorb):  $p_2 = 1$ ;

(c) CO desorption probability (probability that a CO molecule will desorb when a site is selected randomly at a frequency equal to the CO collision frequency and the site is occupied by an adsorbed CO; as defined, this probability is inversely proportional to CO pressure):  $p_3 = 0$ ;

(d) reaction probability (probability that a reaction event will occur when a pair of neighboring sites is selected randomly and the site pair is occupied by one adsorbed CO molecule and one adsorbed O atom):  $p_4 = 0.4$ ;

(e) actions allowed on diagonally adjacent pairs of sites,

(f) stoichiometrically balanced ratio of gas-phase CO and  $O_2$ :  $P_{CO}/P_{O_2} = 2$ .

The differing molecular weights of CO and  $O_2$  were taken into account when determining the relative collision frequencies of these reactants in the simulations.

Reaction rates are reported relative to the CO collision frequency. The results presented here are expected to correspond most closely to reaction over  $Pt/SnO_2$  and  $Pd/SnO_2$  catalysts at room temperature, where the CO sticking probability is near one and the CO desorption probability is near zero. The results presented also apply



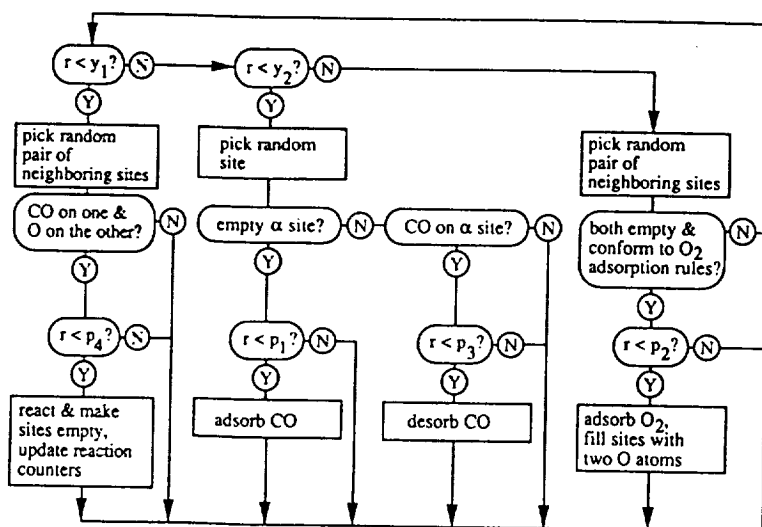


FIG. 1. Main loop in the Monte Carlo simulations.  $r$  = new random number between 0 and 1 generated at each step within the loop.  $y_1$  = fraction of iterations that are checks for reaction =  $y_2$  ( $P_{\text{co,base}}/P_{\text{co}})/(1 + y_2 (P_{\text{co,base}}/P_{\text{co}}))$ , where ( $P_{\text{co,base}}/P_{\text{co}}$ ) is the ratio of the CO partial pressure for the base set of conditions to the CO partial pressure for the specific simulation run.  $y_1$  is defined such that the frequency of checks for reaction in the program at the base set of conditions equals the frequency of CO collisions and such that the frequency of checks for reaction in "real time" is independent of CO pressure.  $y_2$  = fraction of gas molecules colliding with the surface that are CO molecules.  $p_1$  = CO sticking probability.  $p_2$  =  $\text{O}_2$  sticking probability.  $p_3$  = CO desorption probability.  $p_4$  = reaction probability. See text for further explanation of probabilities.

to CO sticking probabilities less than one when the other probabilities and the reaction rate are normalized properly with respect to the CO sticking probability. Here, we refer to the unnormalized probabilities and rates for simplicity.

All simulations were performed starting from a clean surface and run to steady-state conditions. In most cases, steady state was reached within 1000 Monte Carlo steps, where, in one Monte Carlo step, the loop in Fig. 1 is repeated the number of times equal to the total number of sites in the array. Cases which did not reach steady state within about 1000 Monte Carlo steps eventually deactivated completely. All reaction rates reported are average steady-state rates. In most cases, these rates were obtained by starting averaging after attainment of steady state at 3600 Monte Carlo steps into the run and averaging over the subsequent 3900 Monte Carlo steps.

For the parameter values used here, the effect of  $\beta$  sites on  $\alpha$  sites is localized and propagates only a short distance into a "patch" or "particle" of  $\alpha$  sites. Figure 2 shows the variation in reaction rate on  $\alpha$

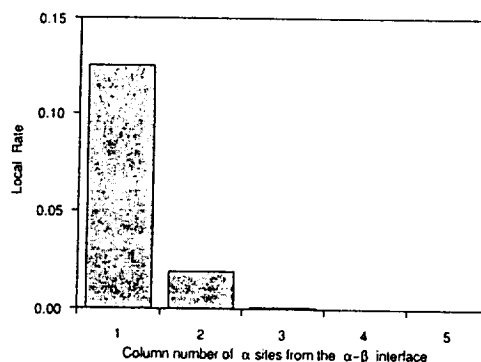


FIG. 2. Local rate vs distance from a semi-infinite linear  $\alpha$ - $\beta$  interface. The local rate is equal to the number of reaction events on an  $\alpha$  site per CO collision with that site.

sites with distance from a semi-infinite  $\alpha$ - $\beta$  interface for the base set of parameters and for a case in which  $O_2$  can adsorb on any pair of neighboring sites. The reaction rate is zero everywhere except for the three columns or rows of  $\alpha$  sites nearest the  $\alpha$ - $\beta$  interface. This result is similar to that obtained by Brosilow *et al.* (9) at  $P_{CO}/P_{O_2} = 2.1$  for adsorption-limited reaction.

#### RANDOM $\alpha$ - $\beta$ SITE DISTRIBUTIONS

A  $42 \times 26$  lattice with 1092 total sites and periodic boundaries was used for the simulations of all- $\alpha$  and random  $\alpha$ - $\beta$  surfaces. Random  $\alpha$ - $\beta$  surfaces represent the opposite extreme in geometric  $\alpha$ - $\beta$  configuration from the noble-metal particles on reducible-oxide supports simulated by Brosilow *et al.* (9). Some Pt-Sn surface alloys have a highly interspersed geometry (42); reaction over other Pt-Sn alloys may involve an intermediate  $\alpha$ - $\beta$  geometry, which might be obtained in simulations by "annealing" initially random surfaces.

For the case in which  $O_2$  can adsorb on any site pair and the CO desorption probability is zero, the reaction rate for the all- $\alpha$  surface is zero. The rate is nonzero for the all- $\alpha$  surface for nonzero CO desorption probabilities. For low CO desorption probabilities, the rate increases dramatically when  $\beta$  sites are added to the surface. The relative increase is inversely related to the CO desorption probability. At ambient temperature over Pd, the CO desorption frequency from a site is on the order of  $10^0 \text{ s}^{-1}$  (7). This desorption frequency leads to a CO desorption probability, as defined above, of  $10^{-7}$  at  $P_{CO} = 0.01 \text{ atm}$ , a CO pressure characteristic of  $CO_2$  TEA lasers (4). With this value of the CO desorption probability, the overall rate increases by 10 orders-of-magnitude—from  $10^{-14}$  reaction events per CO collision with the surface to  $10^{-4}$ —as the fraction of  $\beta$  sites is increased from 0 to 1%. This result demonstrates the extreme sensitivity of steady-state CO oxidation rates over Pd and Pt to the addition of small amounts of an oxygen adsorbing component

that is not inhibited by CO. In an experimental demonstration of a related phenomenon, Mundshau and Rausenberger (47) used photoelectron microscopy to show the presence of defect sites present in low concentration in the surface of single crystal Pt that adsorb CO only weakly and initiate the transient burn-off of inhibiting CO overlayers by  $O_2$ .

A CO desorption probability of zero was used in most of this work in order to simulate the strong CO adsorption on noble metal sites at ambient temperatures and, thus, the strong inhibition of  $O_2$  adsorption on Pt-group noble metals. In general, the absence of reactant desorption and surface diffusion in Monte Carlo simulations produces results which highlight the geometric effects present in the physical system modeled.

The reaction rate is zero for all  $\alpha$ -plus- $\beta$  surfaces with no CO desorption when  $O_2$  adsorption is not allowed on  $\beta$ - $\beta$  pairs. This is because all  $\alpha$  sites are saturated with CO in this case, thus blocking  $O_2$  adsorption on  $\alpha$ - $\alpha$  and  $\alpha$ - $\beta$  pairs. The rate is nonzero with no CO desorption on  $\alpha$ -plus- $\beta$  surfaces when oxygen adsorption is allowed on  $\beta$ - $\beta$  pairs.

We focus on the two cases of adsorption of  $O_2$  on (a) any site pair and (b) only  $\beta$ - $\beta$  site pairs. In each of these two cases, the  $O_2$  sticking probability is the same on all allowed site pairs. In real catalysts, we would expect that the sticking probability would be different on different site pairs. The two cases considered here are limiting cases, with real systems possibly having behavior intermediate between these two cases.

Figure 3 shows the steady-state rate-per- $\alpha$ -site vs the fraction of  $\beta$  sites present in the surface ("fraction- $\beta$ " below). The rate-per- $\alpha$ -site is equal to the average number of reaction events per CO collision with an  $\alpha$  site. In many cases, the noble metal component represented by the  $\alpha$  sites may be the major cost factor in a catalyst. The open circles are for the case in which  $O_2$  can adsorb on any site pair. The solid diamonds are for the case which  $O_2$  can only adsorb

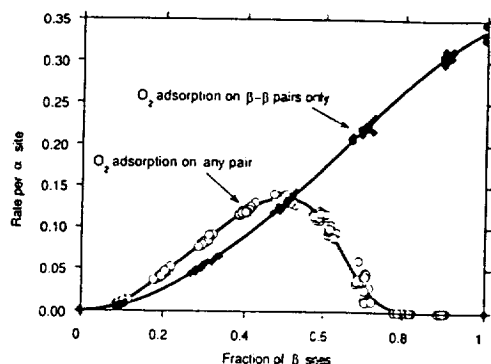


FIG. 3. Steady-state rate-per- $\alpha$ -site vs fraction- $\beta$  for the base set of parameters. The rate-per- $\alpha$ -site is equal to the average number of reaction events per CO collision with an  $\alpha$  site.

on  $\beta$ - $\beta$  pairs. At each nominal fraction- $\beta$ , 20 runs were performed to show the variation in rate from run to run, except for only three runs at fraction- $\beta = 0.99$  for the solid diamonds. At each specific fraction- $\beta$ , the variation in rate is caused by the fact that different random configurations of  $\alpha$  and  $\beta$  sites have somewhat different activities.

For the case in which  $O_2$  adsorption is allowed on  $\beta$ - $\beta$  pairs only, the rate-per- $\alpha$ -site is zero at fraction- $\beta = 0$ , since no  $O_2$  can adsorb, and increases continuously as the fraction of  $\beta$  sites is increased. The rate-per- $\alpha$ -site is somewhat more linear than simply being proportional to the square of the fraction of  $\beta$  sites. The rate-per- $\alpha$ -site approaches a value of 0.33 reaction events per CO collision with an  $\alpha$  site as the fraction of  $\beta$  sites approaches one, that is, in the limit of isolated  $\alpha$  sites surrounded by  $\beta$  sites. In surfaces with high fraction- $\beta$  but before this limit, two widely separated  $\alpha$  sites are more active than two adjoining  $\alpha$  sites but are less active than two  $\alpha$  sites separated by a distance of one or two  $\beta$  sites. In the latter case,  $O_2$  adsorption and reaction are enhanced in the region between the two  $\alpha$  sites since there is an increased rate of formation of vacant  $\beta$ - $\beta$  site pairs in this region.

For the case in which  $O_2$  adsorption is

allowed on any site pair, the rate-per- $\alpha$ -site goes through a maximum at fraction- $\beta = 0.5$ . To the left of the rate maximum, the rate increases as more  $\beta$  sites are added to the surface because  $O_2$  can adsorb on  $\beta$  sites next to CO molecules adsorbed on  $\alpha$  sites. To the right of the rate maximum, the rate-per- $\alpha$ -site decreases as more  $\beta$  sites are added to the surface. This occurs because  $\alpha$  sites are becoming increasingly dispersed among  $\beta$  sites and, thus, are becoming more susceptible to deactivation by irreversibly adsorbed oxygen atoms. These oxygen atoms cannot desorb because the oxygen desorption probability is zero. They cannot be removed by reaction because there are no neighboring  $\alpha$  sites in the local vicinity which are not also deactivated by oxygen.

Figure 4 shows a "snapshot" of the surface for the two cases at fraction- $\beta = 0.5$ . The reaction rates are approximately equal for both cases at this fraction- $\beta$ . Note that there is less CO present on the surface for the case where  $O_2$  can adsorb on any site pair. This is because some  $\alpha$  sites are covered with adsorbed oxygen atoms. Relatively isolated  $\alpha$  sites are deactivated by this adsorbed oxygen. Oxygen adsorbed on  $\alpha$  sites near other  $\alpha$  sites covered with CO can be removed by reaction. At fraction- $\beta = 0.5$ , the deactivation of isolated  $\alpha$  sites by oxygen roughly balances the contribution to reaction by oxygen adsorption on  $\alpha$  sites which remain active. Qualitatively, adsorbed CO and O are interspersed for the case where  $O_2$  can adsorb only on  $\beta$ - $\beta$  pairs, whereas adsorbed CO and O are found primarily in separate patches for the case where  $O_2$  can adsorb on any site pair as a result of the coverage and deactivation of isolated  $\alpha$  sites by adsorbed O.

For the case in which  $O_2$  adsorption is allowed only on neighboring  $\beta$ - $\beta$  pairs, isolated  $\beta$  sites are inactive, of course. Isolated  $\beta$  sites are also inactive for the case in which  $O_2$  adsorption is allowed on any site pair when the CO desorption probability is zero. With a nonzero CO desorption probability for this second case, an isolated  $\beta$  site is

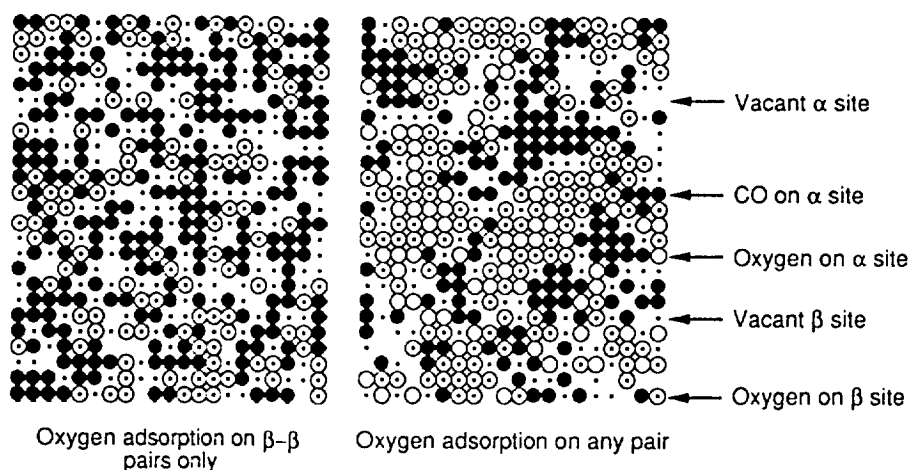


FIG. 4. Instantaneous surface configurations during steady-state reaction for two cases of  $O_2$  adsorption. The fraction of  $\beta$  sites is 0.5 for both cases and the base set of parameters is used. Only parts of the complete surfaces are shown.

active but has a much lower activity than a pair of neighboring  $\beta$  sites. An isolated pair of  $\beta$  sites is active for both cases ( $O_2$  adsorption only on  $\beta$ - $\beta$  pairs,  $O_2$  adsorption on any pair) with no CO desorption. Such an isolated  $\beta$ - $\beta$  pair, however, is more active for the case in which  $O_2$  can adsorb on any site pair since  $O_2$  adsorption can involve a neighboring  $\alpha$  site and one of the  $\beta$  sites, not just the  $\beta$ - $\beta$  pair itself. The height of the solid curve above the dashed curve at low fraction- $\beta$  shows the extent to which  $O_2$  adsorption on  $\alpha$ - $\alpha$  and  $\alpha$ - $\beta$  pairs contributes to the reaction rate for the case in which  $O_2$  adsorption can occur on any site pair. The differences between these two cases decrease as the oxygen sticking probability decreases.

For the case in which  $O_2$  adsorption is allowed on any site pair, note in Fig. 3 that the scatter of rates at a given fraction- $\beta$  is higher at large fraction- $\beta$  than at low fraction- $\beta$ . This scatter at large fraction- $\beta$  is caused by the fact that different proportions of site configurations susceptible to oxygen poisoning are generated at the start of the different runs. The surface becomes completely oxygen poisoned for a fraction of  $\beta$  sites equal to 0.8 and above. The time

required for complete deactivation to occur in these cases is much longer than the normal start-up transient for runs in which the surface remains active.

For the runs shown in Fig. 3, actions involving diagonally adjacent sites are allowed. When "diagonal actions" involving these "diagonal pairs" are not allowed, the reaction rate decreases by about one-third. However, when diagonal actions are not allowed there is no qualitative change in behavior, with one exception: for the case in which  $O_2$  can only adsorb on  $\beta$ - $\beta$  pairs, the rate-per- $\alpha$ -site drops to zero as the fraction of  $\beta$  sites approaches one rather than approaching a nonzero value. That is, individual  $\alpha$  sites surrounded by  $\beta$  sites are inactive at steady state when diagonal actions are not allowed. After an initial transient in which CO adsorbs on these sites and reacts with oxygen atoms which have adsorbed on neighboring  $\beta$  sites, the reaction ceases. This is because oxygen is removed by reaction from the  $\beta$  sites to the left and right and top and bottom of an  $\alpha$  site and this oxygen cannot be replaced. Since, at steady state, the  $\beta$  sites neighboring the  $\alpha$  site diagonally, and essentially all other  $\beta$  sites, are filled with oxygen atoms, these vacant  $\beta$  sites to

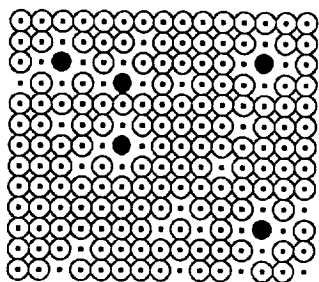


FIG. 5. Instantaneous surface configuration during steady-state reaction for a case in which  $O_2$  can adsorb on  $\beta$ - $\beta$  pairs only; the fraction of  $\beta$  sites on the entire surface is 0.99, and the base set of parameters is used except that actions involving diagonally adjacent pairs of sites are not allowed. All  $\alpha$  sites shown are covered by adsorbed CO, as indicated by the large black circles. The  $\alpha$  site located in the upper left and the two  $\alpha$  sites located on the far right are inactive because  $O_2$  cannot adsorb on the vacant  $\beta$  sites (small black dots) located to their top and bottom and left and right. The two  $\alpha$  sites located just left of center are active since  $O_2$  can adsorb and react on the pair of  $\beta$  sites directly between them.

the left and right and top and bottom do not have any vacant adjacent  $\beta$  sites with which to form a vacant  $\beta$ - $\beta$  pair to allow further  $O_2$  adsorption. This inactive steady-state site configuration is shown in Fig. 5.

Figure 6 shows the same runs plotted in Fig. 3 but now plotted as the "overall rate" vs fraction- $\beta$ . The overall rate is defined as the average number of reaction events per CO collision with any site on the surface. This overall rate corresponds to the rate that would be measured in the laboratory in moles per time per unit BET surface area. Note that both cases show a maximum in overall rate vs fraction- $\beta$ . Although the rate-per- $\alpha$ -site is highest at high fraction- $\beta$  for the case in which  $O_2$  adsorbs only on  $\beta$ - $\beta$  pairs, the overall rate is relatively low because of the low fraction of  $\alpha$  sites. For both cases at low fraction- $\beta$  (0 to 0.3), the overall reaction rate in each case is roughly proportional to the fraction of  $\alpha$  sites times the square of the fraction of  $\beta$  sites. The overall rate for the case in which  $O_2$  adsorbs only on  $\beta$ - $\beta$  pairs continues to be roughly de-

scribed by this proportionality from low to high fraction- $\beta$ .

The results shown in Fig. 6 are in qualitative agreement with the experimental results of Upchurch *et al.* (48). They found that the CO oxidation activity, per unit weight, of a series of Pt/SnO<sub>2</sub> catalysts was highest at intermediate Pt-SnO<sub>2</sub> weight ratios. Surface composition measurements, especially at low noble-metal surface fractions, will be required in future studies in order to distinguish between different  $O_2$  adsorption rules.

#### Alternate Rules for $O_2$ Adsorption

Two different sets of rules for  $O_2$  adsorption were discussed above:  $O_2$  adsorption on any site pair and  $O_2$  adsorption only on  $\beta$ - $\beta$  pairs. The comparison between these two sets of rules demonstrates that, whenever  $O_2$  can adsorb on  $\beta$ - $\beta$  pairs, the predominate mode of reaction involves  $O_2$  adsorption on these pairs, with reaction involving  $O_2$  adsorption on  $\alpha$ - $\beta$  and, especially,  $\alpha$ - $\alpha$  pairs contributing only slightly. The main contribution seen from allowing  $O_2$  adsorption to involve  $\alpha$  sites was to allow for oxygen poisoning of highly dispersed  $\alpha$  sites at high fraction- $\beta$ .

We have also investigated the behavior

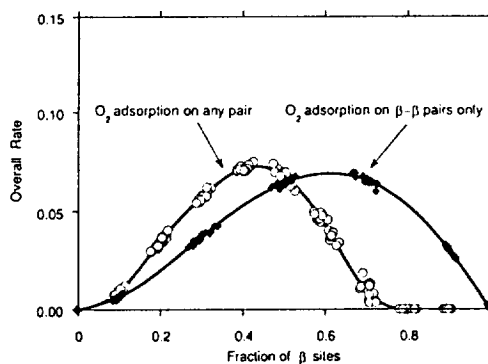


FIG. 6. The same runs in Fig. 3, now plotted as the overall rate vs fraction- $\beta$ . The overall rate shown here is equal to the average number of reaction events per CO collision with any site on the surface. This rate would be proportional to the observed rate per total, or BET, surface area measured experimentally over an actual catalyst.

with other sets of site pairs on which  $O_2$  adsorption is allowed. The case in which  $O_2$  adsorption is allowed on  $\alpha$ - $\beta$  and  $\beta$ - $\beta$  pairs behaves similarly to the case in which  $O_2$  adsorption is allowed on all site pairs.

Two sets of rules were investigated which do not allow  $O_2$  adsorption on  $\beta$ - $\beta$  site pairs:  $O_2$  adsorption only on (a)  $\alpha$ - $\beta$  pairs and (b)  $\alpha$ - $\alpha$  and  $\alpha$ - $\beta$  pairs. For these sets of rules, the surfaces are inactive when the CO desorption probability is zero, since all  $\alpha$  sites are covered by CO, preventing  $O_2$  adsorption. As the CO desorption probability is increased slightly (e.g., to 0.01) from zero, the reaction rate becomes nonzero at most fractions of  $\beta$  sites. With a nonzero CO desorption probability, the rate-per- $\alpha$ -site goes through a maximum at intermediate fraction- $\beta$ . The rate remains low at low fraction- $\beta$  because of CO poisoning of the  $\alpha$  sites in  $\alpha$ - $\alpha$  and  $\alpha$ - $\beta$  site pairs. In many cases, the rate remains zero at high fraction- $\beta$  because of oxygen poisoning of  $\alpha$  sites. Specifically, for  $O_2$  adsorption on  $\alpha$ - $\beta$  pairs only and for a CO desorption probability of 0.01, the rate remains zero at fraction- $\beta = 0.7$  and  $0.9$  for diagonal actions not allowed but is nonzero at these fraction- $\beta$  when diagonal actions are allowed. For  $O_2$  adsorption on  $\alpha$ - $\alpha$  and  $\alpha$ - $\beta$  pairs only and for a CO desorption probability of 0.01, the rate is zero at fraction- $\beta = 0.9$  whether or not diagonal actions are allowed. The effect of allowing diagonal actions is to enhance the reaction rate somewhat, except in the case mentioned above for  $O_2$  adsorption on  $\alpha$ - $\beta$  pairs only where inactive surfaces become active if diagonal actions are allowed.

#### Variation of $O_2$ Sticking Probability

In the simulations presented above, the  $O_2$  sticking probability was set equal to the CO sticking probability, as in the Monte Carlo models of Ziff and co-workers (8, 49). Over noble metals,  $O_2$  sticking probabilities are lower than CO sticking probabilities (50). Here, the effect of reducing the  $O_2$

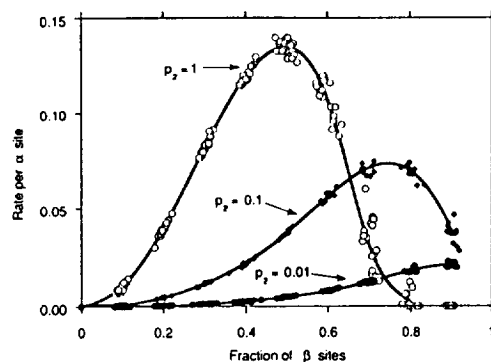


FIG. 7. Variation of  $O_2$  sticking probability,  $p_2$ .  $O_2$  can adsorb on any site pair and the base set of parameters was used except for the variation in  $p_2$ . Note that, as  $p_2$  decreases, the shape of the curve for this case approaches the shape of the curve in Fig. 3 for the case in which  $O_2$  can adsorb on  $\beta$ - $\beta$  pairs only.

sticking probability is investigated for cases in which diagonal actions are allowed.

For the case in which  $O_2$  adsorption is allowed only on  $\beta$ - $\beta$  site pairs, decreasing the  $O_2$  sticking probability decreases the rate at all fraction- $\beta$ . For the case in which  $O_2$  adsorption is allowed on any site pair, decreasing the  $O_2$  sticking probability decreases the rate at low fraction- $\beta$  because of the reduced rate of  $O_2$  adsorption on all site pairs. This behavior is shown in Fig. 7. Decreasing the  $O_2$  sticking probability increases the rate at high fraction- $\beta$  because oxygen poisoning of highly dispersed  $\alpha$  sites is reduced. The surface at fraction  $\beta = 0.8$  goes from inactive to active when the  $O_2$  sticking probability is decreased from 1.0 to 0.5. As a result of this behavior, the rate maximum shifts to higher fraction- $\beta$  and reduces in amplitude as the  $O_2$  sticking probability is decreased. The overall result is that, as the  $O_2$  sticking probability is reduced to lower values, the case in which  $O_2$  adsorption is allowed on any site pair exhibits behavior more similar to the case in which  $O_2$  adsorption is allowed only on  $\beta$ - $\beta$  pairs.

#### Apparent Orders of Reaction

The dependence of the reaction rate on changes in reactant pressure over small

ranges in reactant pressure can be reported in terms of a power-law rate expression. When the CO and O<sub>2</sub> pressures are varied independently, the rate can be expressed as  $r = kP_{\text{CO}}^{\phi}P_{\text{O}_2}^{\gamma}$ . This rate expression is an empirical correlation of results and does not represent a kinetic mechanism, and the reaction orders are not restricted to integer values. For the Monte Carlo results presented here, the apparent order of the reaction with respect to CO was determined by doubling the CO pressure, keeping the O<sub>2</sub> pressure constant and then using the equation

$$\phi = \frac{\ln(r_2/r_1)}{\ln 2}, \quad (1)$$

where  $\phi$  is the apparent order with respect to CO,  $r_1$  is the rate (number of reaction events per unit "real time") at the base CO and O<sub>2</sub> pressures in a stoichiometrically balanced ratio, and  $r_2$  is the rate obtained when the CO pressure was doubled. The apparent order with respect to O<sub>2</sub>,  $\gamma$ , was determined in a similar manner by doubling the O<sub>2</sub> pressure and holding the CO pressure constant.

For a stoichiometrically balanced mixture of CO and O<sub>2</sub>, the rate can be expressed as  $r = kP_{\text{CO}}^{\eta} = k'P_{\text{O}_2}^{\eta}$ , where  $P_{\text{CO}} = 0.5P_{\text{O}_2}$  and where  $\eta$  is the apparent overall order. For the Monte Carlo results presented here, the apparent overall order of the reaction was determined by doubling both the CO and O<sub>2</sub> pressures while keeping the reactant pressure ratio stoichiometrically balanced. The overall order was then determined from the equation

$$\eta = \frac{\ln(r_2/r_1)}{\ln 2}, \quad (2)$$

where  $r_1$  is the rate at the base CO and O<sub>2</sub> pressures in a stoichiometrically balanced mixture, and  $r_2$  is the rate obtained when both the CO and O<sub>2</sub> pressures are doubled. The overall order for a stoichiometric mixture will equal the sum of the individual orders,  $\eta = \phi + \gamma$ , when the overall and

individual orders are determined for infinitesimally small variations in CO and O<sub>2</sub> pressures, or when the true kinetics obey the power-law expression exactly.

There are only a limited number of experimental studies that report the kinetics of the CO oxidation reaction at low temperature over NMRO catalysts. Although these studies have not provided a clear picture of the dependence of rate on reactant pressure, all show that the kinetics are different than those observed over single-component noble-metal catalysts. Stark and Harris (4) determined that the overall order of the reaction was approximately one for stoichiometrically balanced mixtures over Pd/SnO<sub>2</sub> and Pt/SnO<sub>2</sub>, and Badlani (1) obtained the same result over Au/MnO<sub>2</sub>. Over Pd/SnO<sub>2</sub> at low temperature, Bond *et al.* (35) found that the reaction was slightly negative order in CO. They also found that the reaction was approximately half order in O<sub>2</sub> over a range of O<sub>2</sub> concentration which depended on Pd concentration and temperature and tended to zero order at high O<sub>2</sub> concentrations. Sampson and Gudde (51) studied stoichiometric mixtures of CO and O<sub>2</sub> over a "precious metal"-SnO<sub>2</sub> catalyst at low temperature and found that the reaction was zero order in CO and first order in O<sub>2</sub>. Logan and Paffett (42) determined that the reaction was slightly positive order in both CO and O<sub>2</sub> over a 50-50 Pd-Sn surface alloy.

Figure 8 shows the apparent reaction orders vs fraction- $\beta$  for the Monte Carlo simulation case in which O<sub>2</sub> can adsorb on any site pair and for the base set of parameters. One interesting observation is that the overall order for the stoichiometric mixture is roughly constant and equal to 0.5 over most of the range of surface composition. Although the separate orders with respect to CO and O<sub>2</sub> change substantially over this range, these changes compensate each other. At small fraction- $\beta$ , reaction orders are similar to those that would be observed over a noble metal: the rate is positive order in O<sub>2</sub> and negative order in CO due to CO inhibition of O<sub>2</sub> adsorption on  $\alpha$  sites. At

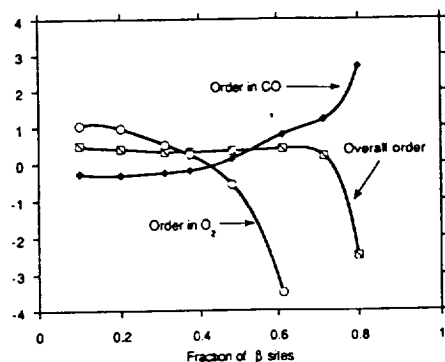


FIG. 8. Reaction orders vs fraction- $\beta$  for the case in which  $O_2$  can adsorb on any site pair and for the base set of parameters.

large fraction- $\beta$ , the apparent orders are determined primarily by changes in oxygen poisoning of relatively isolated  $\alpha$  sites: as the  $O_2$  pressure increases the poisoning becomes more severe and the rate decreases; as the CO pressure increases  $\alpha$  sites become more resistant to oxygen poisoning and the rate increases.

Figure 9 shows how the overall order varies with the  $O_2$  sticking probability. When the  $O_2$  sticking probability is 0.01, the overall order is approximately one, in agreement with most experimental measurements of reaction of stoichiometric mixtures over NMRO catalysts at low temperature (1, 4,

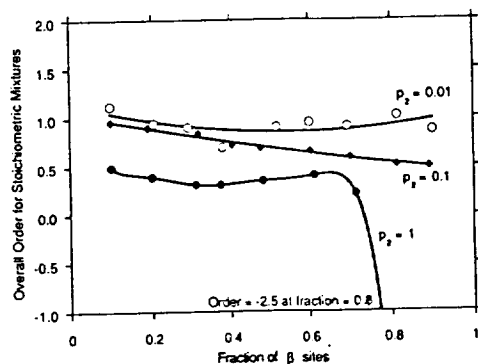


FIG. 9. Effect of varying the  $O_2$  sticking probability,  $p_2$ , on the overall order for the case in which  $O_2$  can adsorb on any site pair and for base set of parameters.

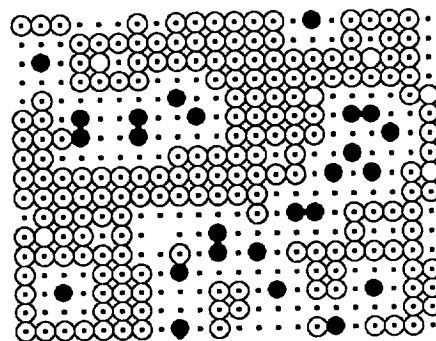


FIG. 10. Instantaneous surface configuration during steady-state reaction for the case in which  $O_2$  can adsorb on any site pair; the fraction of  $\beta$  sites on the entire surface is 0.9, and the base set of parameters is used except that the  $O_2$  adsorption probability,  $p_2$ , equals 0.01.

51), and the reaction is first order in  $O_2$  and zero order in CO, in agreement with the experiments of Sampson and Gudde (51). Figure 10 shows a characteristic configuration of a surface with 90%  $\beta$  sites and an  $O_2$  sticking probability of 0.01. At any given time during steady state, the  $\alpha$  sites are nearly saturated with CO molecules,  $\beta$  sites neighboring  $\alpha$  sites are nearly vacant,  $\beta$  sites far from  $\alpha$  sites are saturated with oxygen. These results predict that the reaction rate is limited by the adsorption of  $O_2$  at (or reoxidation of) reducible oxide sites located at the interface between the noble metal and reducible oxide components.

Figure 11 shows the overall order vs fraction- $\beta$  for the case in which  $O_2$  can adsorb only on  $\beta$ - $\beta$  pairs and for the base set of parameters. Since there is no CO inhibition or oxygen poisoning in this case, the order in CO decreases toward zero and the order in  $O_2$  and the overall order increase toward one as the  $O_2$  sticking probability decreases. At low  $O_2$  sticking probability, the behavior for the two cases of  $O_2$  adsorption rules is similar since  $O_2$  adsorption on  $\alpha$ - $\alpha$  and  $\alpha$ - $\beta$  pairs becomes insignificant for the case in which  $O_2$  can adsorb on any site pair.



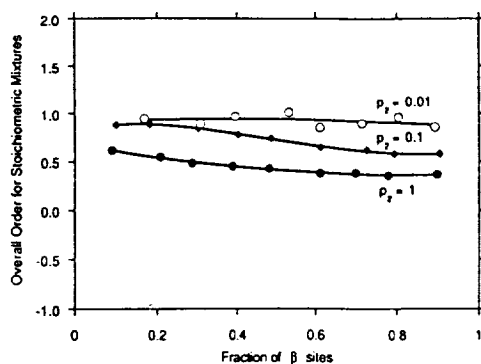


FIG. 11. Effect of varying the  $O_2$  sticking probability,  $p_2$ , on the overall order for the case in which  $O_2$  can adsorb only on  $\beta$ - $\beta$  pairs and for the base set of parameters.

#### Variation of CO Desorption Probability

Over metal catalysts where CO inhibition dominates at low temperature, CO desorption is a critical kinetic step in determining the rate. CO desorption is also the most highly activated step in the mechanism of CO oxidation over metals (7). At relatively high  $P_{CO}/P_{O_2}$ , where the reaction is negative order in CO pressure, the overall reaction rate increases with temperature primarily as a result of an increased rate of CO desorption and a lower inhibiting CO coverage. Thus, apparent activation energies of the overall reaction (42) are in the same range, 80–120 kJ/mol, as the activation energy for CO desorption (7).

CO desorption is less critical over NMRO catalysts than over metals because CO inhibition is less important. Over these NMRO catalysts at relatively high  $P_{CO}/P_{O_2}$ , CO oxidation is only slightly positive (42) or slightly negative order in CO (35) and the apparent activation energies are substantially lower—roughly 20–40 kJ/mol (1, 42)—than for metal catalysts.

The effect of increasing the CO desorption probability from zero was investigated with the Monte Carlo model for cases in which diagonal actions are allowed. For the case in which  $O_2$  adsorption is allowed only on  $\beta$ - $\beta$  site pairs, changing the CO de-

sorption probability from zero to 0.01 produced only a slight decrease in rate at all fraction- $\beta$ . Increasing the CO desorption probability further simply results in further decreases in reaction rate at all fraction- $\beta$ .

For the case in which  $O_2$  adsorption is allowed on any site pair, changing the CO desorption probability slightly from zero to 0.01 causes the all- $\alpha$  surface to become active but results in only slight changes in rate at higher fraction- $\beta$ . As the CO desorption probability increases, the rate at low fraction- $\beta$  increases and the rate at high fraction- $\beta$  decreases such that the rate maximum shifts to lower fraction- $\beta$ . This trend of a shift of the rate maximum to lower fraction- $\beta$  continues as the CO desorption probability is further increased, as shown in Fig. 12.

Continuing with the cases shown in Fig. 12, for a CO desorption probability of 0.3, the surface at fraction- $\beta = 0.7$  has become inactive as more  $\alpha$  sites become susceptible to oxygen poisoning as the CO coverage on these sites decreases with the increase in CO desorption rate. Except for cases such as this in which a surface becomes completely and irreversibly deactivated, the change in rate over a given surface with increase in CO desorption probability is reversible when the CO desorption probability is later decreased.

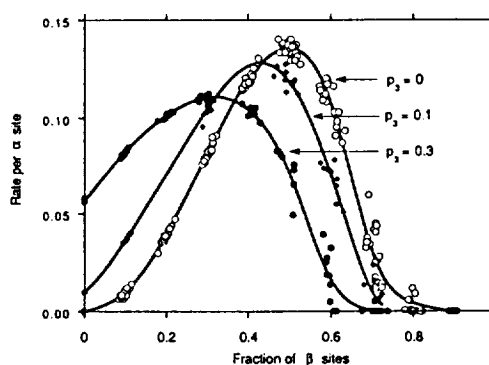


FIG. 12. Variation of CO desorption probability,  $p_3$ .  $O_2$  can adsorb on any site pair and the base set of parameters was used except for the variation in  $p_3$ .

#### SEARCH FOR OPTIMAL SITE CONFIGURATIONS

One question that arises is what the optimal configuration of  $\alpha$  and  $\beta$  sites on the surface is in order to obtain the highest rate-per- $\alpha$ -site or the highest overall rate. One goal, after the correct mechanism is determined, would be the ability to design and prepare the optimal catalyst. Because of the low-temperature operating conditions associated with many of the applications of NMRO CO oxidation catalysts, an optimal but thermodynamically unstable site configuration may be kinetically stable over operating periods of practical length.

One possible way to search for the optimal surface configuration for a given set of rules and parameters would be to take an active site configuration found from a run with a random surface and propagate it periodically across a larger surface. During each run the cumulative number of reaction events occurring on each site was recorded after the start-up transient. This allowed us to look at each surface configuration, search for the most active  $\alpha$  site, for example, and then examine the site configuration surrounding this site. We found that the most active site configurations changed as the rules for  $O_2$  adsorption changed. Figure 13 shows several most-active site configurations at various fraction- $\beta$  for cases in which  $O_2$  can adsorb on any site pair and diagonal actions are allowed. Similar configurations and rates are obtained when diagonal actions are not allowed. For each configuration, the most active  $\alpha$  site is the central site in the surrounding  $7 \times 7$  site array shown. Note that the local  $\alpha$ - $\beta$  ratio and the rate on the most active  $\alpha$  site are roughly constant even though the average  $\alpha$ - $\beta$  ratio and the average rate change substantially between different sets of patterns. Three of the five patterns shown have a local fraction- $\beta$  in the  $3 \times 3$  array of sites centered on the most active  $\alpha$  site = 0.44 (4/9), one pattern has a local fraction- $\beta$  = 0.56 (5/9), and one has a local fraction- $\beta$  = 0.33 (3/9).

Another approach to finding an optimal

site configuration would involve "evolution" of a surface toward a more active configuration. Starting with a random surface of a desired fraction- $\beta$ , for example, the computer program could switch one of the least active  $\alpha$  sites to a  $\beta$  site and one of the least active  $\beta$  sites to an  $\alpha$  site. If this "mutation" resulted in an increase in rate, it would be preserved and another mutation would be tried. If the mutation resulted in a decrease in rate, it would be reversed.

The approach we have pursued most extensively involves searching for optimal periodic configurations of  $\alpha$  and  $\beta$  sites. First we specify the size of a square "base array." Second we choose a fixed number of  $\alpha$  and  $\beta$  sites that will populate this base array. Third, the specified number of  $\alpha$  and  $\beta$  sites are placed in the base array in one of the statistical combinations that are possible. Finally, the base array is propagated periodically and equally in two dimensions for a specified number of repetitions. The resulting square surface is specified to have the conventional periodic boundary conditions with respect to  $O_2$  adsorption and surface reaction. Finally, the reaction is run on the resulting surface and a time-averaged steady-state rate is determined. Results for two of the cases we have studied are reported here: in one case diagonal actions were allowed, and in the other case diagonal actions were not allowed. In both cases  $O_2$  adsorption can occur on any site pair and the base set of parameter values was used.

The smallest possible base array is a  $1 \times 1$  array. The only configurations possible are the all- $\alpha$  surface and the all- $\beta$  surface. These surfaces are also possible surfaces for all larger base arrays and will not be mentioned below. Both of these surfaces are inactive for the two cases considered here.

The next larger base array is a  $2 \times 2$  array. Simulations were performed with surfaces in which the base arrays were propagated periodically eight times in both directions, with the entire  $16 \times 16$  arrays having conventional periodic boundary conditions for reaction and  $O_2$  adsorption. All surfaces

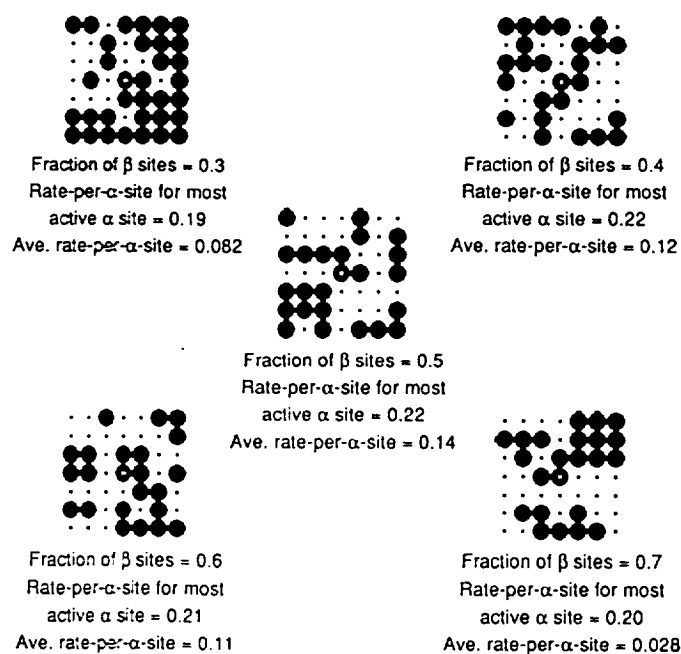


FIG. 13. Sections showing the site configurations surrounding the most active  $\alpha$  sites present in individual random  $\alpha$ - $\beta$  surfaces for the case in which  $O_2$  can adsorb on any site pair and for the base set of parameters.  $\alpha$  sites are represented as large black circles and  $\beta$  sites are represented as small black dots, with adsorbed species not shown. The most active  $\alpha$  site is the central site in each section and is marked with a white dot at its center. For this set of reaction rules and parameter values, the rate-per- $\alpha$ -site for the most active  $\alpha$  sites in random surfaces is about 0.2 at all active fraction- $\beta$ .

with  $2 \times 2$  base arrays were inactive for the two cases considered here, with two exceptions. One exception is a 50–50 mixture of  $\alpha$  and  $\beta$  sites arranged in alternating nondiagonal rows of  $\alpha$  and  $\beta$  sites. This surface is active for the case considered in which diagonal actions are not allowed, and the rate-per- $\alpha$ -site is 0.06. The rate-per- $\alpha$ -site for a 50–50 mixture of  $\alpha$  and  $\beta$  sites arranged randomly is 0.13.

The other exception is a 50–50 mixture of  $\alpha$  and  $\beta$  sites arranged in alternating diagonal rows of  $\alpha$  and  $\beta$  sites, a configuration which looks like a “checkerboard” of  $\alpha$  and  $\beta$  sites. This surface is active for the case considered in which diagonal actions are allowed, and the rate-per- $\alpha$ -site is 0.17, higher than for the 50–50 random surface.

The  $c(2 \times 2)$ -Sn/Pd(100) surface alloys studied experimentally by Logan and Paffett (42) have a checkerboard configuration of Pt

and Sn atoms, as determined by low energy electron diffraction and surface composition measurements. They found that the surface was active for CO oxidation when exposed to 16-Torr CO and 8-Torr  $O_2$  at 170°C, however, the checkerboard structure was disrupted as Sn became oxidized and presumably formed  $SnO_x$  patches on top of the surface. An interesting question is whether the checkerboard Pt–Sn surface alloy would be stable and have a high activity for CO oxidation under milder conditions than used in (42).

The next larger base array is a  $3 \times 3$  array. This base array is sufficiently large that a large number of interesting surface configurations are possible. For each specified ratio of  $\alpha$  and  $\beta$  sites, each distinct configuration of sites is a statistical “combination.” A search of possible statistical combinations of  $\alpha$  and  $\beta$  sites was performed in the follow-

ing manner in order to achieve a confidence limit of >99.9% of trying all nonequivalent combinations: A configuration in the base array which does not have two- or fourfold rotational symmetry is equivalent, with respect to reaction, to the three other distinct statistical combinations that are formed by rotation of this nonrotationally symmetric configuration. By running a number of trials with random generation of site configuration equal to twice the number of possible statistical combinations, at least one of these four equivalent configurations will be tried within a confidence limit of >99.9%. During the same number of trials, at least one of the four equivalent configurations of all combinations which do not have two- or fourfold rotational symmetry will also be tried within this confidence limit. Configurations in the square base arrays that have two- or fourfold rotational symmetry were run deliberately by specifying the site configurations manually in separate runs.

The search for optimal site configurations with  $3 \times 3$  base arrays was performed with surfaces in which the base arrays were propagated periodically seven times in both directions, with the entire  $21 \times 21$  arrays having conventional periodic boundary conditions for reaction and  $O_2$  adsorption.

Figures 14 and 15 summarize the results of the searches performed with  $3 \times 3$  base arrays. Figure 14 is for runs in which diagonal actions are not allowed and Fig. 15 is for runs in which diagonal actions are allowed. The notation below each pattern gives the fraction- $\beta$ , the rate-per- $\alpha$ -site, and rate-per- $\alpha$ -site over a random surface with the same fraction- $\beta$ . The effect of disallowing or allowing diagonal actions on the most active site configurations is clear: in Fig. 14 the  $\alpha$  and  $\beta$  sites tend to be arranged in horizontal and vertical rows, whereas diagonal groupings of  $\alpha$  sites and  $\beta$ - $\beta$  site pairs are prevalent in Fig. 15. Note the similarity between the local configurations of the most active  $\alpha$  sites in random surfaces, shown in Fig. 13, and the optimal  $3 \times 3$  base-array configurations found for the same rules and param-

eters in Fig. 15, especially the lower left configuration.

For the case in which diagonal actions are not allowed, all of the patterns in Fig. 14 are more active than the checkerboard pattern, which is inactive. For the case in which diagonal actions are allowed, all of the patterns in Fig. 15 are less active than the checkerboard pattern.

In Fig. 15, one can form the optimal three- $\beta$ -site pattern simply by adding one  $\beta$  site to the base array of the optimal two- $\beta$ -site pattern. Adding one  $\beta$  site to the base array of the optimal three- $\beta$ -site pattern forms the optimal four- $\beta$ -site pattern, and so forth to form the optimal five- $\beta$ -site pattern. A similar progression can be done in Fig. 14, except that movement of a  $\beta$  site is required to go from the optimal three- $\beta$ -site pattern to the optimal four- $\beta$ -site pattern.

The results of Fig. 3 for random surfaces over which  $O_2$  can adsorb on any site pair can be compared with the results of Fig. 15 for optimal  $3 \times 3$  base-array patterns with the same  $O_2$  adsorption rules. In most cases in which the  $3 \times 3$  patterns are active, they are somewhat more active than a random surface at the same fraction- $\beta$ . The  $3 \times 3$  patterns are inactive below fraction- $\beta = 0.22$  and above fraction- $\beta = 0.56$ , whereas random surfaces are active except at fraction- $\beta = 0$  and at fraction- $\beta = 0.8$  and above.

The rate-per- $\alpha$ -site of the most active  $\alpha$  site was about 0.2 reaction events per CO collision for all random surfaces corresponding to the diagonal-pair rules and fraction- $\beta$  shown in Figs. 14 and 15. This rate is higher than the rates found for the checkerboard pattern and the patterns in the  $3 \times 3$  search. This suggests that a base array larger than the  $3 \times 3$  base array may be required in order to construct the overall optimal pattern of  $\alpha$  and  $\beta$  sites.

The next larger base array is the  $4 \times 4$  base array. We did not do a complete study of  $4 \times 4$  base arrays since the number of possible configurations is very large. From observing the patterns found in the  $3 \times 3$

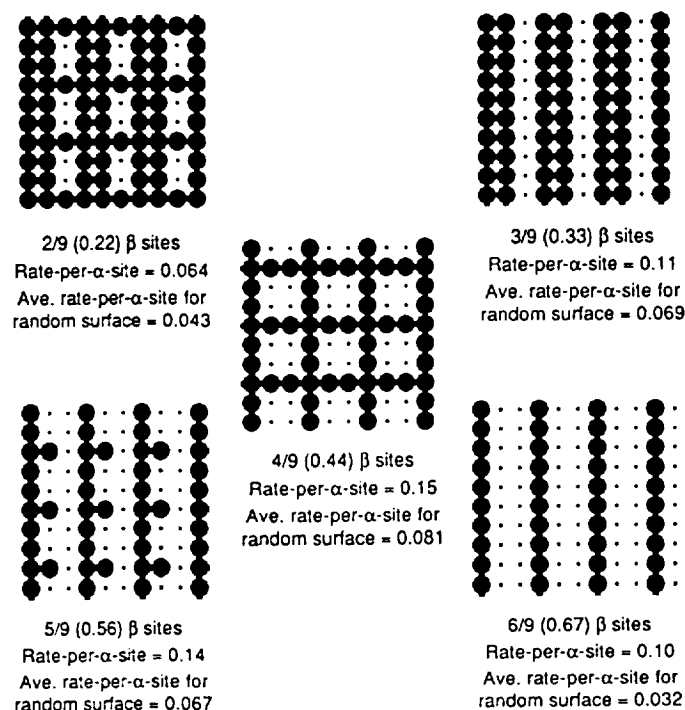


FIG. 14. The most active configurations found for  $3 \times 3$  base arrays for cases in which diagonal actions are not allowed.  $O_2$  can adsorb on any nondiagonal site pair, and the base set of parameters was used with the exception of not allowing diagonal actions.  $\alpha$  sites are represented as large black circles and  $\beta$  sites are represented as small black dots. The case in which there is one  $\beta$  site in the nine-site base array is inactive due to CO poisoning, and the cases in which there are seven or eight  $\beta$  sites in the base array are inactive due to oxygen poisoning of the  $\alpha$  sites.

base array search, we inferred that the  $4 \times 4$  base-array configuration shown in the upper right quadrant of Fig. 16 would have high activity for the case in which diagonal actions are allowed. The rate-per- $\alpha$ -site over this "zig-zag" pattern is higher than any found in the  $3 \times 3$  base array search but is 4% less than over the checkerboard pattern shown in the upper left quadrant of Fig. 16. The zig-zag pattern is probably less active than the checkerboard because an oxygen atom adsorbed on an  $\alpha$  site can be removed by CO molecules adsorbed on other  $\alpha$  sites along only one diagonal direction (i.e., the  $\alpha$  chains are isolated from each other), and a buildup of adsorbed oxygen atoms in one section of an  $\alpha$  chain can lead to deactivation of this section of the chain. In the checkerboard, an oxygen atom ad-

sorbed on an  $\alpha$  site can be removed by CO molecules adsorbed on other  $\alpha$  sites along two diagonal directions.

Adding one  $\alpha$  site to the  $4 \times 4$  base array that forms the zig-zag pattern produces the "zig-zag +  $1\alpha$ " pattern shown in the lower right quadrant of the figure. This pattern has a lower rate-per- $\alpha$ -site than the pattern above it but has the highest overall rate of any surface we have identified. Note that the zig-zag chains of  $\alpha$  sites in the zig-zag +  $1\alpha$  pattern are connected to each other at points every four  $\alpha$ 's along the chains, thus reducing the chance that a section of  $\alpha$  chain will be deactivated by adsorbed oxygen. The "checkerboard +  $1\alpha$ " pattern, formed by adding one  $\alpha$  site to the  $4 \times 4$  base array that forms the checkerboard pattern, is 0.2% less active than the zig-zag +

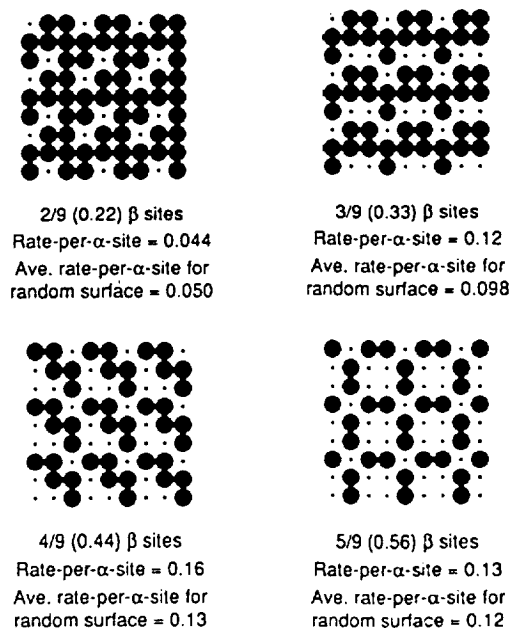


FIG. 15. The most active configurations found for  $3 \times 3$  base arrays for cases in which diagonal actions are allowed.  $O_2$  can adsorb on any site pair, and the base set of parameters was used.  $\alpha$  sites are represented as large black circles and  $\beta$  sites are represented as small black dots. The case in which there is one  $\beta$  site in the nine-site base array is inactive due to CO poisoning, and the cases in which there are six, seven, or eight  $\beta$  sites in the base array are inactive due to oxygen poisoning of the  $\alpha$  sites.

$1\alpha$  pattern. Subtracting one  $\alpha$  site from the  $4 \times 4$  base arrays of the two top patterns in the figure results in decreases in both the rates-per- $\alpha$ -site and the overall rates.

#### SUMMARY

This study demonstrates how high activity for CO oxidation can be obtained over a composite material composed of a highly interspersed mixture of one type of site,  $\alpha$ , that adsorbs CO and  $O_2$  and another type of site,  $\beta$ , that adsorbs  $O_2$  without significant CO inhibition. As long as  $O_2$  can adsorb on a pair of  $\beta$  sites, this mode of  $O_2$  adsorption will predominate at low temperatures, where the CO desorption probability is low, over other possible modes of  $O_2$  adsorption. The main effect of  $O_2$  adsorption on  $\alpha$ - $\alpha$

or  $\alpha$ - $\beta$  pairs is partial deactivation of the surface at high fraction- $\beta$ , and this deactivation will be minimal when the  $O_2$  sticking probability on  $\alpha$  sites is low relative to the CO sticking probability, except at extremely high fraction- $\beta$ . For some reaction rules and parameter values, specific  $\alpha$ - $\beta$  ratios or specific site configurations are inactive. For most reaction rules and parameter values, a roughly 50-50 mixture of the two types of sites will give the greatest activity per unit total surface area. This result is determined

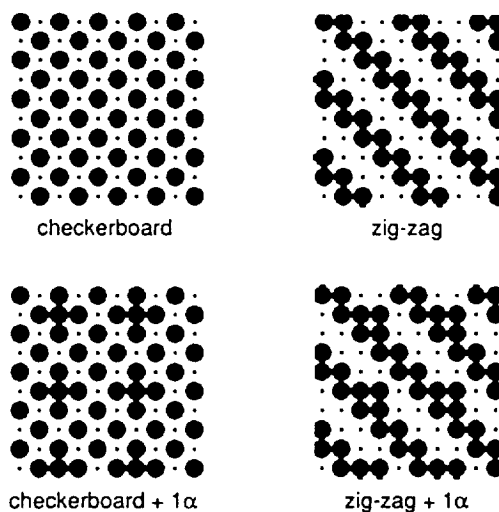


FIG. 16.  $4 \times 4$  base-array patterns with high activity for the case in which  $O_2$  can adsorb on any site pair, diagonal actions are allowed, and the base set of parameters is used. The two top patterns are composed of  $8/16$  (0.5)  $\beta$  sites. The checkerboard pattern (also a  $2 \times 2$  base-array pattern) has the highest rate-per- $\alpha$ -site, 0.174, of any pattern studied in this work. The zig-zag pattern has a rate-per- $\alpha$ -site of 0.167. Random surfaces with this fraction of  $\beta$  sites have an average rate-per- $\alpha$ -site of 0.13. The overall rates for the checkerboard, zig-zag, and random patterns are 0.087, 0.084, and 0.065, respectively. The two bottom patterns are composed of  $7/16$  (0.44)  $\beta$  sites. The two bottom patterns have lower rates-per- $\alpha$ -site but higher overall rates than the two top patterns. The rates-per- $\alpha$ -site for the checkerboard +  $1\alpha$ , the zig-zag +  $1\alpha$ , and random patterns with the same fraction- $\beta$  are 0.1575, 0.1580, and 0.13, respectively. The overall rates for the checkerboard +  $1\alpha$ , the zig-zag +  $1\alpha$ , and random patterns with the same fraction- $\beta$  are 0.08857, 0.08875, and 0.073, respectively. The zig-zag +  $1\alpha$  pattern has the highest overall rate of any pattern studied in this work.

by the reaction stoichiometry and the fact that the two reactants primarily adsorb separately on the two different types of sites.

The sites in a randomly distributed mixture of the two types of sites have widely differing activities which depend on the local site configurations. The local site configurations of the most active sites in a random surface are similar to site configurations found in the search for optimal configurations. The site configurations found in the search for optimal configurations were only about 20% more active than the random surfaces of the same overall composition. This small difference may be due to the relatively simple steric requirements of CO and O<sub>2</sub> adsorption. We expect that similar searches for optimal site configurations will be more fruitful for reactions with more complex steric requirements.

More detailed experimental studies of reaction kinetics over composite catalysts are required in order to advance our understanding of low-temperature CO oxidation. The present work emphasizes the need for measurements of surface composition and surface structure. The use of scanning nanoprobe techniques with model catalyst systems, such as Pd-Sn surface alloys (42), should be especially useful. One particularly interesting question is what the relative contributions are of (a) enhanced reaction at the perimeter of noble-metal particles, predicted by the simulations of Brosilow *et al.* (9) and (b) reaction over highly interspersed mixtures of the two components, the presence of which have been identified experimentally by Hoflund and co-workers (39, 40) and the kinetics of which have been simulated in this work.

#### ACKNOWLEDGMENT

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## APPENDIX I

PROGRAM: Patchwork (Microsoft QuickBasic)

This is the program used for random surfaces.

```
-----
CLS
CLEAR
PRINT "Written by Ajay Badlani and Dr. Richard K. Herz, Chemical"
PRINT "Engineering, Mail Code 0310,"
PRINT "University of California at San Diego, La Jolla, CA 92093-0310,"
PRINT "Phone: (619) 534-6540, internet: rherz@ucsd.edu, bitnet:"
PRINT "rherz@ucsd.bitnet"
PRINT "All rights reserved."
PRINT ""
PRINT "Hit any key to continue:"
INPUT MX
REM define variables
DEFINT A-Z
REM dimension arrays
DIM black%(4) 'pen specification for black ovals (CO) and dots (B sites)
DIM shade%(4) 'pen specification for shaded ovals (O atoms)
DIM rectangle%(4) 'coordinates of oval in subgraphics subroutine
DIM site%(100,100) 'site array, see all set-up subroutines for max.
                    'Ispan% and Jspan% values
DIM rxnarray!(100,100) 'array matching site% that keeps track of no. of
                    'reaction events on each site
DIM SM%(10) 'for subcross subroutine
DIM ST%(10) 'for subcross subroutine
DIM Nrxn!(1000) 'number of reaction events in M (100 MC) time steps
DIM VR!(100) 'used in subran0
REM Specify Parameter Values
yco!=2/3'yco is the mole fraction of CO in the CO-O2 mixture
Mco!=28 'Molecular weight of CO
Mo2!=32 'Molecular weight of O2
y!=1/(1+((1-yco!)/yco!)*SQR(Mco!/Mo2!)) 'Ratio of CO collisions to the
                    'total number of collisions
REM reseed random number generator "RND"
REM use "TIMER," but first convert it to an integer (so can later repeat
REM an old run exactly using same seed)
TSEED!=(TIMER-43201!)*(65536!/86401!) '65536 max integer range, 86401
                    'max sec from midnight
ISEED%=FIX(TSEED!) 'ISEED% should be from -32768 to +32766
RANDOMIZE ISEED%
REM Set up graphics by defining bit patterns for the drawing "pen"
black%(0)=&HFFFF:black%(1)=&HFFFF:black%(2)=&HFFFF:black%(3)=&HFFFF
shade%(0)=&H4422:shade%(1)=&H8811:shade%(2)=&H4422:shade%(3)=&H8811
label00: 'label to re-run program
CLS
PRINT "This is a Monte Carlo simulation of CO oxidation on a surface with"
PRINT "two types of sites, A & B."
PRINT "Empty B sites are marked with dots. Empty A sites are blank."
PRINT "Black circles are CO which adsorb on a single A site only."
PRINT "Grey circles are O atoms. O2 needs two empty sites to adsorb."
PRINT "The input options selected determine whether actions involving"
PRINT "next nearest neighbor sites (on diagonals) can occur and whether"
PRINT "O2 can adsorb on AB pairs, AB & BB pairs, AB & AA pairs, any pair,"
PRINT "or just BB pairs."
```

```

PRINT ""
PRINT "Rate constants are read from the file 'Patchwork Input Data' and"
PRINT "are equal"
PRINT "to the probability that an event will happen when the"
PRINT "corresponding"
PRINT "site-occupancy configuration is chosen randomly."
PRINT ""
PRINT "Output data are written to the file 'Patchwork Output ###' where"
PRINT "### is"
PRINT "an index number assigned automatically. The index number is stored"
PRINT "in the file"
PRINT "'Patchwork Index'."
labelREAD:
PRINT ""
PRINT "TURNING OFF COLOR AND SCREEN SAVER SUGGESTED TO SPEED PROGRAM!!!"
PRINT ""
PRINT "EDIT AND CLOSE file 'Patchwork Input Data' before continuing!"
PRINT ""
PRINT "Hit any key when ready to read input data file:"
INPUT MX
CLS
OPEN "Patchwork Input Data" FOR INPUT AS #1
  INPUT #1,M      '#100 MC steps
  INPUT #1,IX     '0=checker, 1=random, 2=4Ax2B stripe, 3=cross, 4=
                  'Donut, 5= read "Patch OLD sites" file
  INPUT #1,FBsite! 'Nominal fraction of B sites for IX = 1, random
                  'distribution
  INPUT #1,NN     '0 means diagonal actions not allowed
  INPUT #1,BB     '0 for O2 ads on AB pairs, 1=AB & BB, 2=AB & AA, 3=any
                  'pair, 4=BB pairs
  INPUT #1,kcoadsorb! 'Probability CO will adsorb on collision with
                  'an empty A site (use value from 0 to 1)
  INPUT #1,kcodesorb! 'Probability that an adsorbed CO on an A site
                  'will desorb when selected (use value from 0 to 1)
  INPUT #1,koxadsorb! 'Probability that an O2 will adsorb on
'collision with an empty site pair determined by BB (use value from 0 to 1)
  INPUT #1,kreact!  'trys at reaction per CO collision with an A site
CLOSE #1
PRINT "M (# 100 MC time steps) = ",M
PRINT "IX (0=checker,1=random,2=4Ax2B stripe,3=cross,4=Donut,5=old sites)"
PRINT "= ",IX
PRINT "FBsite! (fraction of B sites for IX = 1, random distribution)"
PRINT "=",FBsite!
PRINT "NN (0 means diagonal actions not allowed) = ",NN
PRINT "BB (0 for O2 ads on AB pairs, 1=AB & BB, 2=AB & AA, 3=any pair,"
PRINT "4=BB pairs) = ",BB
PRINT "kcoadsorb! =",kcoadsorb!
PRINT "kcodesorb! =",kcodesorb!
PRINT "koxadsorb! =",koxadsorb!
PRINT "kreact! =",kreact!
PRINT ""
PRINT "For uniform, all A surface, BB needs to be = 2"
PRINT "For IX=5, file 'Patch OLD sites' for I=42, J=26 array must be"
PRINT "present"
PRINT ""
PRINT "Hit 1 to re-read input data, any other key to continue:"
INPUT MX
IF MX=1 THEN GOTO labelREAD

```

```

REM **** RE-activate the next 7 lines by removing leading (') to do SCAN ****
'IX=1 'override input params to get random distribution
'BB=2 'override input params on BB, CHECK TO MAKE SURE THIS IS WHAT
      'YOU WANT!!!!!!
'M=15 'override input params on M, CHECK TO MAKE SURE THIS IS WHAT
      'YOU WANT!!!!!!
'FOR ZII=1 TO 9 '**** TEST (should be 9) ****
'FBsite!=(.1*ZII) 'scan range of FBsite!
REM **** repeat 10 times FOR each value of FBsite! ***
'FOR ZI=1 TO 10 '**** TEST (should be 10) ****
REM *****
REM read index file for output file names
OPEN "Patchwork Index" FOR INPUT AS #1
INPUT #1,indexA
CLOSE #1
REM update index file
OPEN "Patchwork Index" FOR OUTPUT AS #1
indexA=indexA+1
PRINT #1,indexA
CLOSE #1
REM open output file
fileout$="Patchwork Output "+STR$(indexA)
OPEN fileout$ FOR OUTPUT AS #1
PRINT #1,"Patchwork Output ",STR$(indexA)
PRINT #1,""
PRINT #1,"Initial state (0=checker, 1=random, 2=4Ax2B stripe, 3=cross,
4=Donut, 5=old sites) = ",IX
PRINT #1,""
PRINT #1,"FBsite! (fraction of B sites for IX = 1, random distribution)"
PRINT #1,"= ",FBsite!
PRINT #1,""
PRINT #1,"NN (0 means diagonal actions not allowed) = ",NN
PRINT #1,""
PRINT #1,"BB (0 for O2 ads on AB pairs, 1=AB & BB, 2=AB & AA, 3=any pair,"
PRINT #1,"4=BB pairs) = ",BB
PRINT #1,""
PRINT #1,"kcoadsorb! = ",kcoadsorb!
PRINT #1,"kcodesorb! = ",kcodesorb!
PRINT #1,"koxadsorb! = ",koxadsorb!
PRINT #1,"kreact! = ",kreact!
PRINT #1,"yco!=",yco!
PRINT #1,""
PRINT #1,"ISEED% = ",ISEED%
PRINT #1,""
REM set-up initial state
IF IX=0 THEN GOSUB subchecker
IF IX=1 THEN GOSUB subrandom
IF IX=2 THEN GOSUB substripes
IF IX=3 THEN GOSUB subcross
IF IX=4 THEN GOSUB subdonut
IF IX=5 THEN GOSUB subsitefile
REM return from initial state set-up subroutines
REM calculate NStotal! the following way to not exceed integer limit
NStotal!=Ispan%
NStotal!=NStotal!*Jspan%
FAactual!=NASite!/NStotal!
FBactual!=1-FAactual!
REM krxn! is the number of trys at reaction to the total trys

```

```

      krxn!=(y!*kreact!)/(1+(y!*kreact!))
PRINT #1, "The total number of sites =",NStotal!
PRINT #1,"The number of A sites =",NASite!
PRINT #1,"FAactual! = ",FAactual!
PRINT #1,"FBactual! (compare to FBsite! for IX = 1) = ",FBactual!
PRINT #1,"krxn! =",krxn!
PRINT #1,""
PRINT #1,"Rate is no. of reaction events per CO collision with an A site,
PRINT #1, "averaged over 100*NStotal! tries (times through loop).\"
PRINT #1,"Dtime! is the no. of CO collisions per A site from time = 0.\"
PRINT #1,\""
PRINT #1,"Dtime!","", "","Rate"
REM display initial state
CLS
GOSUB subgraphics
REM initialize reaction event counter array
FOR I=1 TO Ispan%
  FOR J=1 TO Jspan%
    rxnarray!(I,J)=0!
  NEXT J
NEXT I
REM start main iteration loop
ON BREAK GOSUB labelBREAK: BREAK ON
FOR KK=1 TO M
  REM initialize reaction event counter
  Nrxn!(KK)=0
  REM Set flag IFF so "RND" will be re-seeded in subran0 every 10 KK (every
  REM 1000 MC steps) on average
  REM in order to increase repetition period of "RND"
  GOSUB subran0
  IF RAN0!<.1 THEN IFF=0
FOR K=1 TO 100 '***** TEST (should be 100) *****
FOR LA=1 TO Ispan% 'split into two loops so don't exceed integer limit with
  'large Ispan%*Jspan%
FOR LB=1 TO Jspan%
  REM Check for a reaction krxn! fraction of the time and for an adsorption-
  REM desorption event (1-krxn!) of the time.
  GOSUB subran0
  IF RAN0!>krxn! THEN GOTO label88 'then look at an adsorption event
  REM check to see if reaction happens
  GOSUB subpairpick
  REM REACT if O on A site and CO on A site
  IF site%(x,y)=2 AND site%(xn%,yn%)=1 THEN
    GOSUB subrxn
    GOTO label10
  END IF
  REM REACT if CO on A site and O on A site
  IF site%(x,y)=1 AND site%(xn%,yn%)=2 THEN
    GOSUB subrxn
    GOTO label10
  END IF
  REM REACT if CO on A site and O on B site
  IF site%(x,y)=1 AND site%(xn%,yn%)=12 THEN
    GOSUB subrxn
    GOTO label10
  END IF
  REM REACT if O on B site and CO on A site
  IF site%(x,y)=12 AND site%(xn%,yn%)=1 THEN

```

```

        GOSUB subrxn
        GOTO label10
    END IF
    GOTO label10
label88:
    REM look at a CO event y! fraction of the time and at an oxygen event
    REM (1-y!) of the time
    GOSUB subran0
    IF RAN0!>y! THEN GOTO label888 'then go look at an oxygen event
        REM check for CO adsorption or desorption
        REM pick random site, site%(x,y)
        GOSUB subran0
        x=INT((Ispan%*RAN0!)+1!)
        GOSUB subran0
        y=INT((Jspan%*RAN0!)+1!)
        IF site%(x,y)=0 THEN
            GOSUB subcoadsorb
            GOTO label10
        END IF
        IF site%(x,y)=1 THEN GOSUB subcodesorb
        GOTO label10
label888:
    REM check to see if O2 adsorbs
    GOSUB subpairpick
    REM ADSORB O if BB<4 and empty A site and empty B site
    IF BB<4 AND site%(x,y)=0 AND site%(xn%,yn%)=10 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB<4 and empty B site and empty A site
    IF BB<4 AND site%(x,y)=10 AND site%(xn%,yn%)=0 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB=1 and empty B site and empty B site
    IF BB=1 AND site%(x,y)=10 AND site%(xn%,yn%)=10 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB=2 and empty A site and empty A site
    IF BB=2 AND site%(x,y)=0 AND site%(xn%,yn%)=0 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB=3 and empty A site and empty A site
    IF BB=3 AND site%(x,y)=0 AND site%(xn%,yn%)=0 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB=3 and empty B site and empty B site
    IF BB=3 AND site%(x,y)=10 AND site%(xn%,yn%)=10 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB=4 and empty B site and empty B site
    IF BB=4 AND site%(x,y)=10 AND site%(xn%,yn%)=10 THEN
        GOSUB suboxadsorb
        GOTO label10

```

```

                END IF
label110:
'GOSUB subgraphics '*** activate by removing leading (') to check logic
                'changes by displaying each trial *****
NEXT LB
NEXT LA
NEXT K
    GOSUB subgraphics
    IF NAsite!=0 THEN GOTO labelSKIP
    REM at this point Nrxn!(KK) equals no. of reaction events in 100!*NStotal!
    REM total times through loop.
    Nrxn!(KK)=Nrxn!(KK)/(100!*NStotal!*(1-krxn!)*y!*FAactual!)
    REM Nrxn!(KK) now equals no. of reaction events per CO collision with an A
    REM site
    Dtime!=KK*100*(1-krxn!)*y! 'Dtime! is total no. of CO collisions per A
                                'site since time = 0
labelSKIP:
    LOCATE 21
    PRINT USING "###_ _ _ #.###^ ^ ^ ^";KK,Nrxn!(KK)
    PRINT #1, USING "###_ _ _ #.###^ ^ ^ ^";Dtime!,Nrxn!(KK)
NEXT KK
labelBREAK:
    REM If allowed to complete FOR-NEXT loop, KK becomes M+1, so reset it to
    REM equal M.
    REM If BREAK sent, don't use incomplete series in average below so reset
    REM anyway.
    KK=KK-1
REM **** DE-activate the next 15 lines by adding leading (') to do SCAN ****
    LOCATE 22
    'PRINT "hit any key to re-display final configuration:"
    'INPUT MX
    GOSUB subgraphics
    LOCATE 21
    PRINT USING "###_ _ _ #.###^ ^ ^ ^";KK,Nrxn!(M)
    PRINT "
    'PRINT "hit any key to continue:
    'INPUT MX
        IF KK>15 THEN MS=KK-14 ELSE MS=1
        LOCATE 1
        PRINT "Rate @ M (# 100*NStotal! trys) ",MS,"to",KK
        FOR KS=MS TO KK
            PRINT USING "###^ ^ ^ ^";Nrxn!(KS)
        NEXT KS
REM *****
REM ave the last half of the run to get an average rate
    Avestart%=INT(.5*KK) 'start averaging 50% through series - can change
                        'factor if desired
    Nrxn!(M+1)=0 'place holder for the average of (KK+1-Avestart) Nrxn! to
                'average together
    FOR KS=Avestart% TO KK
        Nrxn!(M+1)=Nrxn!(M+1)+Nrxn!(KS)/(KK+1-Avestart%)
    NEXT KS
    LOCATE 22
    PRINT "Rate =",Nrxn!(M+1)
GOSUB subanalysis
REM finish writing to output file
    PRINT #1,"The following is a 'snapshot' of the final site configuration,"
    PRINT #1,"site%(I,J),"

```

```

PRINT #1," listed as all Jspan% J's for I=1, then all Jspan% J's for I=2,"
PRINT #1,"etc., up to I=Ispan%"
PRINT #1,"Ispan% = ",Ispan%
PRINT #1,"Jspan% =",Jspan%
FOR I=1 TO Ispan%
FOR J=1 TO Jspan%
    PRINT #1,site%(I,J)
NEXT J
NEXT I
PRINT #1,""
PRINT #1,"The following is the reaction event counter array"
PRINT #1,"rxnarray!(I,J),"
PRINT #1," listed as all Jspan% J's for I=1, then all Jspan% J's for I=2,"
PRINT #1,"etc., up to I=Ispan%:"
FOR I=1 TO Ispan%
FOR J=1 TO Jspan%
    PRINT #1,rxnarray!(I,J)
NEXT J
NEXT I
PRINT #1,""
PRINT #1,"END OF DATA"
CLOSE #1
REM update summary file
OPEN "Patchwork Summary" FOR APPEND AS #1

PRINT #1, USING "###_,#####_,_ #_,_ #.###_,_ #_,_ #_,_ #.###^_#_,_
#.###_,_ #.###_,_ #.###_,_
#.###";indexA,ISEED%,IX,FBactual!,NN,BB,Nrxn!(M+1),kcoadsorb!,kcodesorb!,kcxad
sorb!,kreact!

CLOSE #1
REM **** RE-activate next 2 lines by removing leading (') to do a SCAN
*****
'NEXT ZI
'NEXT ZII
REM **** DE-activate next 7 lines by adding leading (') to do a SCAN
*****
LOCATE 21
PRINT "
PRINT "
PRINT "ENTER 1 TO RERUN:
PRINT "
INPUT MX
IF MX=1 GOTO label100
REM *****
BREAK OFF
END
subran0:
REM This routine is similar "RAN0" in the book "Numerical Recipes (FORTRAN) by
REM W. H. Press, et al."
REM It "scrambles" the "RND" numbers to cut down on pair correlations.
REM I have also added a random re-seeding of "RND" to increase its repetition
REM period
REM from originally on the order of 5E07 calls (11,000 MC steps for 1092
REM array).
IF IFF=0 THEN
    IFF=1
    REM re-seed "RND" randomly with random seed to to increase its

```

```

    REM repetition period
    ZR%=32767*RND
    IF RND<.5 THEN ZR%=-ZR%
    RANDOMIZE ZR%
    REM the next lines "set up" the scrambling array for RAN0
    FOR JR=1 TO 97
        dum!=RND
    NEXT JR
    FOR JR=1 TO 97
        VR! (JR)=RND
    NEXT JR
    YR!=RND
END IF
JR=1+INT(97!*YR!)
YR!=VR! (JR)
RAN0!=YR!
VR! (JR)=RND
RETURN
subchecker:
    REM initialize for A-B checker board initial state
    Ispan%=42 'can be changed for different array size but needs to be
               'even number
    Jspan%=26 'can be changed for different array size but needs to be
               'even number
    NAsite!=Ispan%/2
    NAsite!=NAsite!*Jspan% 'calculate this way so don't exceed integer
                           'limit during calculation
    FOR I=1 TO 21 '1 to (Ispan%/2)
        IO=(2*I)-1
        IE=(2*I)
        FOR J=1 TO 13 '1 to (Jspan%/2)
            JO=(2*J)-1
            JE=(2*J)
            site%(IO,JO)=0 'site is empty A site
            site%(IE,JE)=0 'site is empty A site
            site%(IO,JE)=10 'site is empty B site
            site%(IE,JO)=10 'site is empty B site
        NEXT J
    NEXT I
    RETURN
subrandom:
    REM initialize for empty random A-B site distribution
    NAsite!=0!
    Ispan%=42 'can be changed for different array size
    Jspan%=26 'can be changed for different array size
    FOR I=1 TO Ispan%
        FOR J=1 TO Jspan%
            GOSUB subran0
            IF RAN0!>FBSite! THEN
                site%(I,J)=0 'site is empty A site
                NAsite!=NAsite!+1! 'number of A sites to use in
                                   'calculating rate per A site
                GOTO labelSR0
            END IF
            site%(I,J)=10 'site is empty B site
        NEXT J
    labelSR0:
        NEXT J
    NEXT I

```



```

RETURN
substripes:
  REM initialize for stripes of 4 A sites wide followed by 2 B sites wide
  Ispan%=42 'can be changed for different array size but must be
            'multiple of repeat period of 6
  Jspan%=26 'can be changed for different array size
  NAsite!=Jspan%*(4*Ispan%/6)
  FOR I=0 TO 6 '0 to ((Ispan%/6)-1)
    FOR J=1 TO Jspan%
      site%((I*6)+1,J)=0 'site is empty A site
      site%((I*6)+2,J)=0 'site is empty A site
      site%((I*6)+3,J)=0 'site is empty A site
      site%((I*6)+4,J)=0 'site is empty A site
      site%((I*6)+5,J)=10 'site is empty B site
      site%((I*6)+6,J)=10 'site is empty B site
    NEXT J
  NEXT I
RETURN
subcross:
  REM initialize for staggered crosses of A's
  Ispan%=40 'can be changed but must be multiple of repeat period of 8
  Jspan%=24 'can be changed but must be multiple of repeat period of 8
  NAsite!=600 '600 is for Ispan%=40, Jspan%=24
            '(= Ispan%*Jspan%*10/16 ????)
  REM initialize arrays
  SM%(1)=0
  SM%(2)=0
  SM%(3)=0
  SM%(4)=10
  SM%(5)=0
  SM%(6)=10
  SM%(7)=0
  SM%(8)=10
  ST%(1)=1
  ST%(2)=4
  ST%(3)=7
  ST%(4)=2
  ST%(5)=5
  ST%(6)=8
  ST%(7)=3
  ST%(8)=6
  FOR J=0 TO 2 '0 to (Jspan%/8)-1
    FOR JX=1 TO 8
      FOR I=0 TO 4 '0 to (Ispan%/8)-1
        FOR IX=1 TO 8
          CX=ST%(JX)+IX
          IF CX>8 THEN CX=CX-8
          site%((I*8+IX),(J*8+JX))=SM%(CX)
        NEXT IX
      NEXT I
    NEXT JX
  NEXT J
RETURN
subdonut:
  REM initialize for A-B checker board initial state
  Ispan%=42 'can be changed for different array size
  Jspan%=26 'can be changed for different array size
  NAsite!=Ispan%/2

```

```

        NASite!=NASite!*Jspan% 'calculate this way so that it doesnot exceed
                                'integer limit during calculation
FOR I=1 TO 21 '1 to Ispan%/2
FOR J=1 TO 26
site%(I,J)=0 ' site is empty A site
NEXT J
NEXT I
FOR I= 22 TO 42 'Ispan%/2 to Ispan%
FOR J= 1 TO 26
site%(I,J)=10 'site is a empty B site
NEXT J
NEXT I
RETURN
subsitefile:
REM This is set up to read the array "snapshot" of a previous run for an
REM I=42, J=26 array.
REM The file "Patch OLD sites" must be present.
Ispan%=42 'can be changed for different array size
Jspan%=26 'can be changed for different array size
NASite!=0
OPEN "Patch OLD sites" FOR INPUT AS #2
FOR I=1 TO 42
FOR J=1 TO 26
INPUT#2,site%(I,J)
IF site%(I,J)=0 THEN NASite!=NASite!+1
IF site%(I,J)=1 THEN site%(I,J)=0:NASite!=NASite!+1
IF site%(I,J)=2 THEN site%(I,J)=0:NASite!=NASite!+1
IF site%(I,J)=12 THEN site%(I,J)=10
NEXT J
NEXT I
CLOSE #2
RETURN
subpairpick:
REM this picks a random pair of sites
REM pick random site, site%(x,y)
GOSUB subran0
x=INT((Ispan%*RAN0!)+1!)
GOSUB subran0
y=INT((Jspan%*RAN0!)+1!)
REM pick neighboring site
IF NN=0 THEN GOTO labelDD
REM the following 7 lines are for: diagonal neighbor actions are CK
labelNN:
GOSUB subran0
xn%=x+INT(3*RAN0!)-1
GOSUB subran0
yn%=y+INT(3*RAN0!)-1
IF xn%=x AND yn%=y THEN GOTO labelNN 'neighbor can't be itself
GOTO label999
labelDD:
REM the following 18 lines are for: diagonal actions not allowed
GOSUB subran0
IF RAN0!<.5 THEN GOTO label99
xn%=x
GOSUB subran0
IF RAN0!<.5 THEN
    yn%=y+1
ELSE

```

```

        yn%=y-1
    END IF
    GOTO label999
label99:
    yn%=y
    GOSUB subran0
    IF RAN0!<.5 THEN
        xn%=x+1
    ELSE
        xn%=x-1
    END IF
label999:
    REM Set indices correctly for neighbors over array boundary.
    REM This corresponds to the surface as a torus or as a semi-infinite
    REM flat
    REM surface formed of a periodic array of the sub-array computed here.
    IF xn%=0 THEN xn%=Ispan%
    IF xn%>Ispan% THEN xn%=1
    IF yn%=0 THEN yn%=Jspan%
    IF yn%>Jspan% THEN yn%=1
    RETURN
subcoadsorb:
    GOSUB subran0
    IF RAN0!<kcoadsorb! THEN site%(x,y)=1
    RETURN
subcodesorb:
    GOSUB subran0
    IF RAN0!<kcodesorb! THEN site%(x,y)=0
    RETURN
suboxadsorb:
    GOSUB subran0
    IF RAN0!<koxadsorb! THEN
        site%(x,y)=site%(x,y)+2
        site%(xn%,yn%)=site%(xn%,yn%)+2
    END IF
    RETURN
subrxn:
    GOSUB subran0
    IF RAN0!>=.4052345# THEN GOTO labelRXN
    Nrxn!(KK)=Nrxn!(KK)+1!
    IF site%(x,y)=1 THEN site%(x,y)=0
    IF site%(x,y)=2 THEN site%(x,y)=0
    IF site%(x,y)=12 THEN site%(x,y)=10
    IF KK>36 THEN rxnarray!(x,y)=1+rxnarray!(x,y)
    IF site%(xn%,yn%)=1 THEN site%(xn%,yn%)=0
    IF site%(xn%,yn%)=2 THEN site%(xn%,yn%)=0
    IF site%(xn%,yn%)=12 THEN site%(xn%,yn%)=10
    IF KK>36 THEN rxnarray!(xn%,yn%)=1+rxnarray!(xn%,yn%)
labelRXN:
    RETURN
subgraphics:
    FOR I=1 TO Ispan%
    FOR J=1 TO Jspan%
        REM set coordinates for "ovals" (circles here) in PAINTOVAL calls
        rectangle%(0)=(J-1)*12
        rectangle%(1)=(I-1)*12
        rectangle%(2)=J*12
        rectangle%(3)=I*12

```

```

dot%(0)=((J-1)*12)+5
dot%(1)=((I-1)*12)+5
dot%(2)=(J*12)-5
dot%(3)=(I*12)-5
REM update site graphics
IF site%(I,J)=0 THEN 'site is empty A site
    CALL ERASEOVAL(VARPTR(rectangle%(0)))
    GOTO labelGR1
END IF
IF site%(I,J)=1 THEN 'site is CO ads on A site
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(rectangle%(0)))
    GOTO labelGR1
END IF
IF site%(I,J)=2 THEN 'site is O ads on A site
    CALL PENPAT(VARPTR(shade%(0)))
    CALL PAINTOVAL(VARPTR(rectangle%(0)))
    GOTO labelGR1
END IF
IF site%(I,J)=10 THEN 'site is empty B site
    CALL ERASEOVAL(VARPTR(rectangle%(0)))
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(dot%(0)))
    GOTO labelGR1
END IF
IF site%(I,J)=12 THEN 'site is O ads on B site
    CALL PENPAT(VARPTR(shade%(0)))
    CALL PAINTOVAL(VARPTR(rectangle%(0)))
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(dot%(0)))
    GOTO labelGR1
END IF
PRINT "error: in subgraphics with unknown site configuration"
'shouldn't reach this point
labelGR1:
    NEXT J
    NEXT I
RETURN
subanalysis:
    REM determine fractional coverages and statistics
    sumco!=0
    sumox!=0
    FOR I=1 TO Ispan%
        FOR J=1 TO Jspan%
            IF site%(I,J)=1 THEN sumco!=sumco!+1!
            IF site%(I,J)=2 THEN sumox!=sumox!+1!
        NEXT J
    NEXT I
    IF NASite!=0 THEN
        thetaco!=999!
        thetaox!=999!
        GOTO labelANAL1
    END IF
    thetaco!=sumco!/NASite!
    thetaox!=sumox!/NASite!
labelANAL1:
    PRINT #1,"Thetas on A sites ONLY of 'snapshot' of final
configuration:"

```

Appendix I, Program Patchwork Listing, 13 pages total

```
PRINT #1,""  
PRINT #1,USING "_t_h_e_t_a_ _C_O_ _=" "#.####";thetaco!  
PRINT #1,USING "_t_h_e_t_a_ _O_X_ _=" "#.####";thetaox!  
RETURN
```

## APPENDIX II

PROGRAM: Opt?(?)/3x3x7 (Microsoft QuickBasic)

This is the program used for searching for optimal surface structures.

```
-----
CLS
CLEAR
  PRINT "Written by Richard K. Herz, Chemical Engineering, Mail Code 0310,"
  PRINT "University of California at San Diego, La Jolla, CA 92093-0310,"
  PRINT "Phone: (619) 534-6540, internet: rherz@ucsd.edu, bitnet:"
  PRINT "rherz@ucsd.bitnet"
  PRINT "All rights reserved."
  PRINT ""
  PRINT "Hit any key to continue:"
  INPUT MX
REM define variables
DEFINT A-Z
REM dimension arrays
DIM black%(4) 'pen specification for black ovals (CO) and dots (B sites)
DIM shade%(4) 'pen specification for shaded ovals (O atoms)
DIM rectangle%(4) 'coordinates of oval in subgraphics subroutine
DIM site%(100,100) 'site array, see all set-up subroutines for max.
Ispan% and Jspan% values
DIM maxsite%(100,100) 'site array to hold optimal configuration
DIM site0%(100,100)
DIM Nrnxn!(1000) 'number of reaction events in M (100 MC) time steps
DIM VR!(100) 'used in subran0
REM Specify Parameter Values
yco!=2/3 'yco is the mole fraction of CO in the CO-O2 mixture
Mco!=28 'Molecular weight of CO
Mo2!=32 'Molecular weight of O2
y!=1/(1+((1-yco!)/yco!)*SQR(Mco!/Mo2!))
REM y! = Ratio of CO collisions to the total number of collisions
REM reseed random number generator "RND"
REM use "TIMER," but first convert it to an integer
REM (so can later repeat an old run exactly using same seed)
TSEED!=(TIMER-43201!)*(65536!/86401!)
      REM 65536 max integer range, 86401 max sec from midnight
ISEED%=FIX(TSEED!) 'ISEED% should be from -32768 to +32766
RANDOMIZE ISEED%
REM Set up graphics by defining bit patterns for the drawing "pen"
black%(0)=&HFFFF:black%(1)=&HFFFF:black%(2)=&HFFFF:black%(3)=&HFFFF
shade%(0)=&H4422:shade%(1)=&H8811:shade%(2)=&H4422:shade%(3)=&H8811
CLS
PRINT "This is a Monte Carlo simulation of CO oxidation on a surface with"
PRINT "two types of sites, A & B."
PRINT "Empty B sites are marked with dots. Empty A sites are blank."
PRINT "Black circles are CO which adsorb on a single A site only."
PRINT "Grey circles are O atoms. O2 needs two empty sites to adsorb."
PRINT "The input options selected determine whether actions involving"
PRINT "next nearest neighbor sites (on diagonals) can occur and whether"
PRINT "O2 can adsorb on AB pairs, AB & BB pairs, AB & AA pairs, any pair,"
PRINT "or just BB pairs."
PRINT ""
PRINT ""
PRINT "TURNING OFF MONITOR COLOR AND SCREEN SAVER IS SUGGESTED TO SPEED UP
PROGRAM!!!!"
```

```

PRINT ""
PRINT "Hit any key when ready to read input data:"
INPUT MX
CLS
labelASK01:
PRINT "Enter no. of A sites in base array (NABase%):"
INPUT NABase%
PRINT "Enter NN (0 diag no allowed, 1 diag OK):"
INPUT NN
PRINT "NABase% =",NABase%
PRINT "NN = ",NN
PRINT "Enter 2 if you want to revise, any other key to continue:"
INPUT MX
IF MX=2 GOTO labelASK01
M=100 'number of 100 MC steps performed
avestart%=10 'number of runs from start to skip in getting average rate
IX=1
BB=3
kcoadsorb!=1
kcodesorb!=0
koxadsorb!=1
kreact!=1
I0span%=3 'size of base array in I0span direction
J0span%=3 'size of base array in J0span direction
expander%=7 'number of times base array repeated in each direction
REM krxn! is the number of trys at reaction to the total trys
krxn!=(y!*kreact!)/(1+y!*kreact!)
REM set up name of output file
Mtitle$=CHR$(NABase%+48)
Ntitle$=CHR$(NN+48)
Ititle$=CHR$(I0span%+48)
Jtitle$=CHR$(J0span%+48)
Etitle$=CHR$(expander%+48)
fileout$="Opt"+Mtitle$+"("Ntitle$+")/"+Ititle$+"x"+Jtitle$+"x"+Etitle$+"C"
REM print to screen
PRINT "M (# 100 MC time steps) = ",M
PRINT "avestart% = ",avestart%
PRINT "IX (1=random) = ",IX
PRINT "NN (0 means diagonal actions not allowed) = ",NN
PRINT "BB (0 for C2 ads on AB pairs, 1=AB & BB, 2=AB & AA, 3=any pair,"
PRINT "4=BB pairs) = ",BB
PRINT "kcoadsorb! =",kcoadsorb!
PRINT "kcodesorb! =",kcodesorb!
PRINT "koxadsorb! =",koxadsorb!
PRINT "kreact! =",kreact!
PRINT ""
PRINT "I0span%, J0span% = ",I0span%,J0span%
PRINT "NABase% = ",NABase%
PRINT "expander% = ",expander%
PRINT ""
labelASK00:
PRINT "Enter 1 to start with new random array, 2 to read old file,"
PRINT "3 to input manually:"
INPUT MZ
IF MZ<1 OR MZ>3 THEN PRINT "TRY AGAIN":GOTO labelASK00
REM set-up initial state
IF MZ=1 THEN GOSUB subrandom
IF MZ=2 THEN GOSUB suboldfile

```

```

      IF MZ=3 THEN GOSUB submanual
      GOSUB subexpand
      REM calculate NStotal! the following way to not exceed integer limit
      REM during calculation
      NStotal!=Ispan%
      NStotal!=NStotal!*Jspan%
      FAactual!=NAsite!/NStotal!
      FBactual!=1-FAactual!
      REM initialize parameters and write to ouput file so run type recorded if all
      REM poison
      maxrate!=0
      runnum!=0
      GOSUB suboutput
      labelSTART:
      OPEN "OPT Index" FOR INPUT AS #1
      INPUT #1,indexA
      CLOSE #1
      REM update index file
      OPEN "OPT Index" FOR OUTPUT AS #1
      indexA=indexA+1
      PRINT #1,indexA
      CLOSE #1
      runnum!=runnum!+1
      IF runnum!>1 THEN
        GOSUB subrandom 'generate new random surface for next run
        GOSUB subexpand
        REM calculate NStotal! the following way to not exceed integer limit
        REM during calculation
        NStotal!=Ispan%
        NStotal!=NStotal!*Jspan%
        FAactual!=NAsite!/NStotal!
        FBactual!=1-FAactual!
      END IF
      CLS
      GOSUB subgraphics
      REM start main iteration loop
      ON BREAK GOSUB labelBREAK:BREAK ON
      FOR KK=1 TO M
        REM initialize reaction event counter
        Nrnxn!(KK)=0
        REM Set flag IFF so "RND" will be re-seeded in subran0 every 10 KK (every
        REM 1000 MC steps) on average
        REM in order to increase repetition period of "RND"
        GOSUB subran0
        IF RAN0!<.1 THEN IFF=0
      FOR K=1 TO 100
      FOR LA=1 TO Ispan% 'split so don't exceed integer limit in Ispan%*Jspan%
      FOR LB=1 TO Jspan%
        REM Check for a reaction krxn! fraction of the time and for an adsorption-
        REM desorption event (1-krxn!) of the time.
        GOSUB subran0
        IF RAN0!>krxn! THEN GOTO label88 'then look at an adsorption event
        REM check to see if reaction happens
        GOSUB subpairpick
        REM REACT if O on A site and CO on A site
        IF site%(x,y)=2 AND site%(xn%,yn%)=1 THEN
          GOSUB subrxn
          GOTO label110

```



```

        END IF
    REM REACT if CO on A site and O on A site
    IF site%(x,y)=1 AND site%(xn%,yn%)=2 THEN
        GOSUB subrxn
        GOTO label10
    END IF
    REM REACT if CO on A site and O on B site
    IF site%(x,y)=1 AND site%(xn%,yn%)=12 THEN
        GOSUB subrxn
        GOTO label10
    END IF
    REM REACT if O on B site and CO on A site
    IF site%(x,y)=12 AND site%(xn%,yn%)=1 THEN
        GOSUB subrxn
        GOTO label10
    END IF
    GOTO label10
label88:
    REM look at a CO event y! fraction of the time and at an oxygen event (1-
    REM y!) of the time
    GOSUB subran0
    IF RAN0!>y! THEN GOTO label888 'then go look at an oxygen event
    REM check for CO adsorption or desorption
    REM pick random site, site%(x,y)
    GOSUB subran0
    x=INT((Ispan%*RAN0!)+1!)
    GOSUB subran0
    y=INT((Jspan%*RAN0!)+1!)
    IF site%(x,y)=0 THEN
        GOSUB subcoadsorb
        GOTO label10
    END IF
    IF site%(x,y)=1 THEN GOSUB subcodesorb
    GOTO label10
label888:
    REM check to see if O2 adsorbs
    GOSUB subpairpick
    REM ADSORB O if BB<4 and empty A site and empty B site
    IF BB<4 AND site%(x,y)=0 AND site%(xn%,yn%)=10 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB<4 and empty B site and empty A site
    IF BB<4 AND site%(x,y)=10 AND site%(xn%,yn%)=0 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB=1 and empty B site and empty B site
    IF BB=1 AND site%(x,y)=10 AND site%(xn%,yn%)=10 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB=2 and empty A site and empty A site
    IF BB=2 AND site%(x,y)=0 AND site%(xn%,yn%)=0 THEN
        GOSUB suboxadsorb
        GOTO label10
    END IF
    REM ADSORB O if BB=3 and empty A site and empty A site

```

```

        IF BB=3 AND site%(x,y)=0 AND site%(xn%,yn%)=0 THEN
            GOSUB subboxadsorb
            GOTO label10
        END IF
    REM ADSORB 0 if BB=3 and empty B site and empty B site
    IF BB=3 AND site%(x,y)=10 AND site%(xn%,yn%)=10 THEN
        GOSUB subboxadsorb
        GOTO label10
    END IF
    REM ADSORB 0 if BB=4 and empty B site and empty B site
    IF BB=4 AND site%(x,y)=10 AND site%(xn%,yn%)=10 THEN
        GOSUB subboxadsorb
        GOTO label10
    END IF
label10:
'GOSUB subgraphics '*** activate by removing leading (') to check logic
NEXT LB
NEXT LA
NEXT K
    GOSUB subgraphics
    IF NAsite!=0 THEN PRINT "NAsite! = 0 !!!!!!!!!!!!!!!":GOTO labelSKIP
    REM at this point Nrnx!(KK) equals no. of reaction events in 100!*NStotal!
    REM total times through loop.
    Nrnx!(KK)=Nrnx!(KK)/(100!*(1-krxn!)*y!*NAsite!)
    REM Nrnx!(KK) now equals (no. of reaction events per A site) per (CO
    REM collision per A site)
    Dtime!=KK*100*(1-krxn!)*y!
    REM Dtime! is total number CO collisions per A site since time = 0
labelSKIP:
    LOCATE 21
    PRINT fileout$
    PRINT USING "###_ _ _ #.###^";KK,Nrnx!(KK)
    REM ***** TERMINATE RUNNING ON DEAD SURFACE *****
    IF Nrnx!(KK)=0 AND kcodesorb!=0 THEN GOTO labelSTART
    IF Nrnx!(KK)=0 THEN
        killcheck%=0
        FOR I=1 TO Ispan%
            FOR J=1 TO Jspan%
                IF site%(I,J)=0 OR site%(I,J)=1 THEN killcheck%=1
            NEXT J
        NEXT I
    END IF
    REM kill if no vacant or CO-filled A sites left
    IF Nrnx!(KK)=0 AND killcheck%=0 THEN GOTO labelSTART
    REM ***** SURFACE STILL ALIVE IF GET TO HERE *****
NEXT KK
    REM If allowed to complete FOR-NEXT loop, KK becomes M+1, so reset it to
    REM equal M.
    KK=KK-1
    REM average rates calculated after startup period
    Nrnx!(M+1)=0 'place holder for the ave of (KK+1-Avestart) Nrnx!
    FOR KS=(startup%+1) TO KK
        Nrnx!(M+1)=Nrnx!(M+1)+Nrnx!(KS)/(KK-startup%)
    NEXT KS
    LOCATE 22
    PRINT fileout$
    PRINT "Ave. Rate =",Nrnx!(M+1)
    REM ***** check to see if this is the highest rate so far *****

```

```

      IF Nrxn!(M+1)>maxrate! THEN
        maxrate!=Nrxn!(M+1)
        FOR I=1 TO Ispan%
          FOR J=1 TO Jspan%
            maxsite%(I,J)=site%(I,J)
          NEXT J
        NEXT I
        BREAK OFF
        GOSUB suboutput
      END IF
GOTO labelSTART
labelBREAK:
  BREAK OFF
  GOSUB submaxgraph
  LOCATE 22
labelASK:
  PRINT "Continue Program? (y or Y OR n or N):"
  INPUT MY$
  IF MY$="y" OR MY$="Y" THEN GOTO labelSTART
  IF MY$<>"n" AND MY$<>"N" THEN CLS:LOCATE 12:GOTO labelASK
  OPEN fileout$ FOR APPEND AS #1
  PRINT #1,"Total runs started in this set = ",runnum!
  PRINT #1,""
  PRINT #1,"END OF DATA"
  CLOSE #1
END
subran0:
REM This routine is similar "RAN0" in the book "Numerical Recipes (FORTRAN) by
REM W. H. Press, et al."
REM It "scrambles" the "RND" numbers to cut down on pair correlations.
REM I have also added a random re-seeding of "RND" to increase its repetition
REM period
REM from originally on the order of 5E07 calls (11,000 MC steps for 1092 REM
REM array).
  IF IFF=0 THEN
    IFF=1
    REM re-seed "RND" randomly with random seed to to increase its
    REM repetition period
    ZR%=32767*RND
    IF RND<.5 THEN ZR%=-ZR%
    RANDOMIZE ZR%
    REM the next lines "set up" the scrambling array for RAN0
    FOR JR=1 TO 97
      dum!=RND
    NEXT JR
    FOR JR=1 TO 97
      VR!(JR)=RND
    NEXT JR
    YR!=RND
  END IF
  JR=1+INT(97!*YR!)
  YR!=VR!(JR)
  RAN0!=YR!
  VR!(JR)=RND
  RETURN
subrandom:
  REM initialize for empty random A-B site distribution
  labelsR1:

```

```

NA%=0
FBsite!=1-(NAbase%/(I0span%*J0span%))
FOR I=1 TO I0span%
  FOR J=1 TO J0span%
    GOSUB subran0
    IF RAND!>FBsite! THEN
      site0%(I,J)=0:NA%=NA%+1 'site is empty A site
      GOTO labelSR0
    END IF
    site0%(I,J)=10 'site is empty B site
  labelSR0:
  NEXT J
NEXT I
IF NA%<>NAbase% THEN GOTO labelSR1 'fixes no. A sites in base array
RETURN
suboldfile:
CLS
labelASK1:
filename$=FILES$(1,"TEXT")
IF filename$="" GOTO labelASK1
PRINT "Input File is ";filename$
OPEN filename$ FOR INPUT AS #1
PRINT ""
MX=25
FOR I=1 TO MX
  LINE INPUT #1,dummy$
NEXT I
LINE INPUT #1,maxrate$
PRINT maxrate$
MX=5
FOR I=1 TO MX
  LINE INPUT #1,dummy$
  PRINT dummy$
NEXT I
PRINT "hit any key to continue"
INPUT MZZ
FOR I=1 TO I0span%
  FOR J=1 TO J0span%
    INPUT #1,site0%(I,J)
    IF site0%(I,J)=1 THEN site0%(I,J)=0
    IF site0%(I,J)=2 THEN site0%(I,J)=0
    IF site0%(I,J)=12 THEN site0%(I,J)=10
    PRINT "site0%(I,J)=",site0%(I,J)
  NEXT J
NEXT I
CLOSE #1
PRINT "enter any key to continue"
INPUT MX
CLS
FOR IM=0 TO (expander%-1)
FOR JM=0 TO (expander%-1)
FOR I=1 TO I0span%
FOR J=1 TO J0span%
  REM set coordinates for "ovals" (circles here) in PAINTOVAL calls
  rectangle%(0)={(JM*J0span%)+J-1}*12
  rectangle%(1)={(IM*I0span%)+I-1}*12
  rectangle%(2)={(JM*J0span%)+J}*12
  rectangle%(3)={(IM*I0span%)+I}*12

```

```

dot%(0)=(((JM*I0span%)+J-1)*12)+5
dot%(1)=(((IM*I0span%)+I-1)*12)+5
dot%(2)=(((JM*J0span%)+J)*12)-5
dot%(3)=(((IM*I0span%)+I)*12)-5
REM show current maximum rate site configuration
IF site0%(I,J)=0 THEN 'site is empty A site
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(rectangle%(0)))
    GOTO labelOGR1
END IF
IF site0%(I,J)=1 THEN 'site is CO ads on A site
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(rectangle%(0)))
    GOTO labelOGR1
END IF
IF site0%(I,J)=2 THEN 'site is O ads on A site
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(rectangle%(0)))
    GOTO labelOGR1
END IF
IF site0%(I,J)=10 THEN 'site is empty B site
    CALL ERASEOVAL(VARPTR(rectangle%(0)))
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(dot%(0)))
    GOTO labelOGR1
END IF
IF site0%(I,J)=12 THEN 'site is O ads on B site
    CALL ERASEOVAL(VARPTR(rectangle%(0)))
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(dot%(0)))
    GOTO labelOGR1
END IF
PRINT "error: in subgraphics with unknown site configuration"
REM shouldn't reach this point
labelOGR1:
    NEXT J
    NEXT I
    NEXT JM
    NEXT IM
LOCATE 18
PRINT maxrate$
PRINT ""
PRINT "hit any key to continue:"
INPUT MX
RETURN
submanual:
labelMAN:
CLS
PRINT "This is for base array =",I0span%,J0span%
PRINT "With # A sites =",NAbase%
PRINT "Input rows down first column, then second, then third,"
PRINT "A's are 0, B's are 10:"
basecheck%=0
FOR I=1 TO I0span%
    FOR J=1 TO J0span%
        INPUT site0%(I,J)
        IF site0%(I,J)=0 THEN basecheck%=basecheck%+1
    NEXT J

```

```

NEXT I
CLS
FOR IM=0 TO (expander%-1)
FOR JM=0 TO (expander%-1)
FOR I=1 TO I0span%
FOR J=1 TO J0span%
    REM set coordinates for "ovals" (circles here) in PAINTOVAL calls
    rectangle%(0)=((JM*J0span%)+J-1)*12
    rectangle%(1)=((IM*I0span%)+I-1)*12
    rectangle%(2)=((JM*J0span%)+J)*12
    rectangle%(3)=((IM*I0span%)+I)*12
    dot%(0)=((JM*I0span%)+J-1)*12)+5
    dot%(1)=((IM*I0span%)+I-1)*12)+5
    dot%(2)=((JM*J0span%)+J)*12)-5
    dot%(3)=((IM*I0span%)+I)*12)-5
    REM show current maximum rate site configuration
    IF site0%(I,J)=0 THEN 'site is empty A site
        CALL PENPAT(VARPTR(black%(0)))
        CALL PAINTOVAL(VARPTR(rectangle%(0)))
    END IF
    IF site0%(I,J)=10 THEN 'site is empty B site
        CALL ERASEOVAL(VARPTR(rectangle%(0)))
        CALL PENPAT(VARPTR(black%(0)))
        CALL PAINTOVAL(VARPTR(dot%(0)))
    END IF
NEXT J
NEXT I
NEXT JM
NEXT IM
LOCATE 18
IF NABase%<>basecheck% THEN PRINT "NOT THE CORRECT NUMBER OF A SITES"
PRINT "Enter 2 to revise, any other to accept:"
INPUT MX
IF MX=2 GOTO labelMAN
RETURN
subexpand:
NASite!=expander%*expander%*NABase%
Ispan%=I0span%*expander%
Jspan%=J0span%*expander%
FOR IM=0 TO (expander%-1)
    FOR JM=0 TO (expander%-1)
        FOR I=1 TO I0span%
            FOR J=1 TO J0span%
                site%((IM*I0span%)+I,(JM*J0span%)+J)=site0%(I,J)
            NEXT J
        NEXT I
    NEXT JM
NEXT IM
RETURN
suboutput:
OPEN fileout$ FOR OUTPUT AS #1
PRINT #1,fileout$
PRINT #1,""
PRINT #1,"Runs tried to this point =",runnum!
PRINT #1,""
PRINT #1,"Initial state (1=random) = ",IX
PRINT #1,""
PRINT #1,"NN (0 means diagonal actions not allowed) = ",NN

```

```

PRINT #1, ""
PRINT #1, "BB (0 for O2 ads on AB pairs, 1=AB & BB, 2=AB & AA, 3=any"
PRINT #1, "pair, 4=BB pairs) = ", BB
PRINT #1, ""
PRINT #1, "kcoadsorb = ", kcoadsorb!
PRINT #1, "kcodesorb = ", kcodesorb!
PRINT #1, "koxadsorb = ", koxadsorb!
PRINT #1, "kreact! = ", kreact!
PRINT #1, "yco!=", yco!
PRINT #1, ""
PRINT #1, "The total number of sites =", NStotal!
PRINT #1, "The number of A sites =", NASite!
PRINT #1, "FAactual! = ", FAactual!
PRINT #1, "FBactual! (compare to FBsite! for IX = 1) = ", FBactual!
PRINT #1, "krxn! =", krxn!
PRINT #1, ""
PRINT #1, "Maxrate! is no. reactions per CO collision with an A site"
PRINT #1, "averaged over last 24 of 28 X 100 MC steps"
PRINT #1, ""
PRINT #1, "Maxrate!", maxrate!
PRINT #1, ""
PRINT #1, "The following is the site configuration, site0%(I,J),"
PRINT #1, " listed as all J0span% J's for I=1, then all J0span% J's"
PRINT #1, " for I=2, etc., up to I=I0span%"
PRINT #1, "I0span% = ", I0span%
PRINT #1, "J0span% = ", J0span%
FOR I=1 TO I0span%
  FOR J=1 TO J0span%
    PRINT #1, site0%(I,J)
  NEXT J
NEXT I
PRINT #1, ""
CLOSE #1

RETURN
subpairpick:
  REM this picks a random pair of sites
  REM pick random site, site%(x,y)
  GOSUB subran0
  x=INT((Ispan%*RAN0!)+1!)
  GOSUB subran0
  y=INT((Jspan%*RAN0!)+1!)
  REM pick neighboring site
  IF NN=0 THEN GOTO labelDD
  REM the following 7 lines are for: diagonal neighbor actions are OK
labelNN:
  GOSUB subran0
  xn%=x+INT(3*RAN0!)-1
  GOSUB subran0
  yn%=y+INT(3*RAN0!)-1
  IF xn%=x AND yn%=y THEN GOTO labelNN 'neighbor can't be itself
  GOTO label999
labelDD:
  REM the following 18 lines are for: diagonal actions not allowed
  GOSUB subran0
  IF RAN0!<.5 THEN GOTO label99
  xn%=x
  GOSUB subran0
  IF RAN0!<.5 THEN

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        yn%=y+1
    ELSE
        yn%=y-1
    END IF
    GOTO label999
label99:
    yn%=y
    GOSUB subran0
    IF RAN0!<.5 THEN
        xn%=x+1
    ELSE
        xn%=x-1
    END IF
label999:
    REM Set indices correctly for neighbors over array boundary.
    REM Corresponds to the surface as a torus or as a semi-infinite flat
    REM surface formed of a periodic array of the sub-array computed here.
    IF xn%=0 THEN xn%=Ispan%
    IF xn%>Ispan% THEN xn%=1
    IF yn%=0 THEN yn%=Jspan%
    IF yn%>Jspan% THEN yn%=1
    RETURN
subcoadsorb:
    GOSUB subran0
    IF RAN0!<kcoadsorb! THEN site%(x,y)=1
    RETURN
subcodesorb:
    GOSUB subran0
    IF RAN0!<kcodesorb! THEN site%(x,y)=0
    RETURN
suboxadsorb:
    GOSUB subran0
    IF RAN0!<koxadsorb! THEN
        site%(x,y)=site%(x,y)+2
        site%(xn%,yn%)=site%(xn%,yn%)+2
    END IF
    RETURN
subrxn:
    GOSUB subran0
    IF RAN0!>=.4052345+ THEN GOTO labelRXN
    Nrxn!(KK)=Nrxn!(KK)+1!
    IF site%(x,y)=1 THEN site%(x,y)=0
    IF site%(x,y)=2 THEN site%(x,y)=0
    IF site%(x,y)=12 THEN site%(x,y)=10
    IF site%(xn%,yn%)=1 THEN site%(xn%,yn%)=0
    IF site%(xn%,yn%)=2 THEN site%(xn%,yn%)=0
    IF site%(xn%,yn%)=12 THEN site%(xn%,yn%)=10
labelRXN:
    RETURN
subgraphics:
    FOR I=1 TO Ispan%
    FOR J=1 TO Jspan%
        REM set coordinates for "ovals" (circles here) in PAINTOVAL calls
        rectangle%(0)=(J-1)*12
        rectangle%(1)=(I-1)*12
        rectangle%(2)=J*12
        rectangle%(3)=I*12
        dot%(0)=((J-1)*12)+5

```



```

dot%(1)=((I-1)*12)+5
dot%(2)=(J*12)-5
dot%(3)=(I*12)-5
REM update site graphics
IF site%(I,J)=0 THEN 'site is empty A site
    CALL ERASEOVAL(VARPTR(rectangle%(0)))
    GOTO labelGR1
END IF
IF site%(I,J)=1 THEN 'site is CO ads on A site
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(rectangle%(0)))
    GOTO labelGR1
END IF
IF site%(I,J)=2 THEN 'site is O ads on A site
    CALL PENPAT(VARPTR(shade%(0)))
    CALL PAINTOVAL(VARPTR(rectangle%(0)))
    GOTO labelGR1
END IF
IF site%(I,J)=10 THEN 'site is empty B site
    CALL ERASEOVAL(VARPTR(rectangle%(0)))
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(dot%(0)))
    GOTO labelGR1
END IF
IF site%(I,J)=12 THEN 'site is O ads on B site
    CALL PENPAT(VARPTR(shade%(0)))
    CALL PAINTOVAL(VARPTR(rectangle%(0)))
    CALL PENPAT(VARPTR(black%(0)))
    CALL PAINTOVAL(VARPTR(dot%(0)))
    GOTO labelGR1
END IF
PRINT "error: in subgraphics with unknown site configuration"
REM shouldn't reach this point
labelGR1:
    NEXT J
    NEXT I
RETURN
submaxgraph:
    CLS
    FOR I=1 TO Ispan%
    FOR J=1 TO Jspan%
        REM set coordinates for "ovals" (circles here) in PAINTOVAL calls
        rectangle%(0)=(J-1)*12
        rectangle%(1)=(I-1)*12
        rectangle%(2)=J*12
        rectangle%(3)=I*12
        dot%(0)=((J-1)*12)+5
        dot%(1)=((I-1)*12)+5
        dot%(2)=(J*12)-5
        dot%(3)=(I*12)-5
        REM show current maximum rate site configuration
        IF maxsite%(I,J)=0 THEN 'site is empty A site
            CALL PENPAT(VARPTR(black%(0)))
            CALL PAINTOVAL(VARPTR(rectangle%(0)))
            GOTO labelMGR1
        END IF
        IF maxsite%(I,J)=1 THEN 'site is CO ads on A site
            CALL PENPAT(VARPTR(black%(0)))

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```

        CALL PAINTOVAL(VARPTR(rectangle%(0)))
        GOTO labelMGR1
    END IF
    IF maxsite%(I,J)=2 THEN 'site is O ads on A site
        CALL PENPAT(VARPTR(black%(0)))
        CALL PAINTOVAL(VARPTR(rectangle%(0)))
        GOTO labelMGR1
    END IF
    IF maxsite%(I,J)=10 THEN 'site is empty B site
        CALL ERASEOVAL(VARPTR(rectangle%(0)))
        CALL PENPAT(VARPTR(black%(0)))
        CALL PAINTOVAL(VARPTR(dot%(0)))
        GOTO labelMGR1
    END IF
    IF maxsite%(I,J)=12 THEN 'site is O ads on B site
        CALL ERASEOVAL(VARPTR(rectangle%(0)))
        CALL PENPAT(VARPTR(black%(0)))
        CALL PAINTOVAL(VARPTR(dot%(0)))
        GOTO labelMGR1
    END IF
    PRINT "error: in subgraphics with unknown site configuration"
REM shouldn't reach this point
    labelMGR1:
        NEXT J
        NEXT I
    LOCATE 18
    PRINT fileouts
    PRINT "Total number runs started = ",runnum!
    PRINT "Current optimal surface (big black dots are A sites,small dots"
    PRINT "are B sites)"
    PRINT "Max. Rate =",maxrate!
RETURN

```